INSTRUMENTAL METHODS OF ANALYSIS

by

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PREFACE

This book is an outgrowth of the lectures and laboratory work of the courses in Instrumental Methods of Analysis given at the University of Michigan and at Indiana University. For a long time the laboratory directions for the courses have been merely mimeographed notes. The theoretical work was largely presented by lectures, there being no one adequate text. The present book is an attempt to gather many of the theoretical and practical aspects into one text.

The courses given at the two above-mentioned Universities are primarily introductory courses in the use of instrumental or physico-chemical methods in analytical chemistry. They are designed to survey the vast field of instrumentation and give the student an idea of the types of instruments available, the theory behind their operation, the limitations, advantages and disadvantages of each instrument and a brief summary of the applications. It is not expected that the student will become an expert by any means after this introductory course. References to more complete works are therefore given for each instrument or method.

This book has been written in considerable haste in order that it might appear in time for student use in the fall of 1948. It is, therefore, incomplete in many respects, e.g., among others, polarimetry is not included. There are, undoubtedly, many errors and it is hoped that all users of the book will call the authors' attention to these errors so that they may be corrected at the earliest opportunity. In a field which is changing so rapidly, no book can be completely up-to-date, and an early revision is planned. The laboratory directions have been in use for some time in the authors' classes and should be reliable. Suggestions for additional experiments would be welcomed.

The selection of the particular make or makes of instruments to be described in each case has been governed largely by those which happen to be available at the University of Michigan and at Indiana University. This does not mean that these particular makes are the best. Each user of instruments must decide for himself which make will perform best under his particular set of conditions. It is hoped that the instrument makers will send descriptions and photographs of their devices to be included, if possible, in later editions.

It has been difficult to condense into one volume the great amount of theoretical material on the instruments chosen for this book. Great use has been made of the existing literature and the main sources of information are included at the end of each chapter. Many readers will object to the use of the word "instrument" or "instrumental" when referring to some of the material in this book. Until better words appear, however, these words must suffice.

The authors wish to express their thanks to Dr. T. Y. Toribara for assistance in preparing a portion of the text.

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CHAPTER I

VISUAL COLORIMETERS
FUNDAMENTAL LAWS OF COLORIMETRY

The colorimeter is an instrument which compares the light transmitted by a solution with that transmitted by a standard solution. The simplest instruments may consist of little more than two matched tubes, whereas more complicated devices may employ photoelectric tubes as measuring devices for the light. The solutions employed need not necessarily be true solutions; colloidal solutions are sometimes employed if they appear clear. When the particles of the solute are too large the solutions appear turbid, and instruments which depend on the measurement of the light scattered or absorbed by turbid solutions are known as turbidimeters or nephelometers. These latter instruments will be discussed in Chapter III.

Absorption of Radiant Energy. When a beam of light or radiant energy passes through a medium, as, for example, a colored solution, some of the energy may be absorbed by the molecules of the medium. The beam emerging from the medium then has less energy than when it entered and some of the light is spoken of as having been absorbed. It should be remembered that visible light represents only a small part of the electromagnetic spectrum. Visible light consists of waves having wavelengths from about 4000 Å to 8000 Å (1 Å = 10^{-8} cm.). All electromagnetic energy seems to occur in discrete bundles, called photons or quanta, which have energies proportional to the frequency of the radiation. Thus,

$$E = h\nu \qquad (1)$$

where E represents energy in ergs, ν, frequency in cycles per second, and h is a universal constant known as Planck's constant and has the value 6.624×10^{-27} erg-sec. Ultraviolet radiation with short wavelengths or high frequencies has higher energy content and infrared radiation with long wavelengths or low frequencies has lower energy content.

Molecules are capable of interaction with radiant energy, photons, in several ways. Three important methods are (1) the energy of the photon is consumed in increasing rotational energy of the molecule, (2) the energy of the photon is employed to increase both the energy of vibration and rotation of the molecule, (3) the energy of the photon is used to excite an electron or electrons of the molecule to higher energy levels and also perhaps to increase the energy of vibration and rotation of the molecules. Process (1) requires less energy than (2); process (3) requires the greatest amount of energy. Molecules of different substances differ in the energy required for each of the processes. Furthermore, there may be many different changes possible in each process. Thus photons of certain frequencies (energy contents) are absorbed by some molecules, and photons of different frequencies may be absorbed by other molecules. This leads to absorption spectra which are characteristic of each type of molecule. The determination of the absorption spectra of substances is considered in a later chapter.

In this chapter the determination of concentration by the amount of light absorbed at some fixed wavelength or over a fixed region of wavelengths will be considered.

Definition of Terms and Symbols. Before going farther, it might be well to define several of the terms which are used in colorimetric work.[1]

Brightness is that attribute of any color with respect to which it may be classed as equivalent to some member of a series of grays, ranging from white to black.

Hue is that attribute which distinguishes a color as reddish, yellowish, greenish, bluish, etc.

Purity denotes the degree of redness, yellowness, greenness, blueness, etc. The ultimate purity would be a light beam consisting of rays of one and only one wavelength.

Colorimetry is the determination of the concentration of a substance by measurement of the relative absorption or transmittancy of the material. The term colorimetry has also been used to specify the characteristics of a colored substance, but this latter meaning will not be used in this book.

In addition to the above terms there are a large number of other terms which are frequently represented by symbols. The symbols most used are defined below.

1. See reports of the Committee on Colorimetry, Optical Society of America, J. Optical Soc. Am., 33, 544 (1943); 34, 183, 245, 633 (1944); 35, 1 (1945).

A = absorption = 1 - T.

c = concentration. In chemical colorimetry c is frequently measured in g./liter or mg./ml.

D = optical density = E = extinction

$$= \log_{10} \frac{I_o}{I}.$$

$$E = \text{extinction} = \log_{10} \frac{I_o}{I}.$$

$E^{1\%}_{1cm.}$ = extinction or optical density of a 1 cm. layer of solution containing 1% by weight of solute = $\frac{1}{pl} \log \frac{I_o}{I}$.

I_o = intensity of light transmitted by pure solvent, or, intensity of light entering the solution.

I = intensity of light beam emerging from the solution or transmitted by the solution.

k = specific extinction coefficient = $\frac{E}{cl}$

$$= \frac{1}{cl} \log \frac{I_o}{I}.$$

l = length of absorbing layer of material = cm.

M = molecular weight.

p = percentage of solute = g./100 g.

T = transmittancy = $\frac{I}{I_o}$.

%T = percentage transmittancy = $100 \frac{I}{I_o}$ = 100 T.

ε = molecular extinction coefficient

$$= Mk = \frac{1}{\frac{cl}{M}} \log \frac{I_o}{I}.$$

When dealing with the wavelength or frequency of light, certain other terms are used. The common methods of expressing this property of light and the relationships between the various units are given below.

A or Å = angstrom unit, a unit of wavelength = $\frac{1}{6{,}438.4696}$ of wavelength of red Cd line $\doteq 10^{-8}$ cm.

c = velocity of light = 3.997×10^{10} cm./sec.

f = Fresnel unit, a unit of frequency = $10^{-12} \times \nu$ = vibrations per 10^{-12} sec.

m μ = millimicron, a unit of wavelength = 10^{-7} cm. = 10 Å.

λ = wavelength (in cm. unless otherwise specified).

μ = micron, unit of wavelength = 10^{-3} mm. = 10^{-4} cm.

ν = frequency = vibrations/sec.

$\bar{\nu}$ = wave number = vibrations/cm. = $\frac{1}{\lambda}$.

Transformations involving the six quantities, $\nu, \bar{\nu}$, f, m μ, μ, Å are given in the Appendix.

Fundamental Laws of Colorimetry. There are two fundamental laws underlying the practice of colorimetry. They are Bouguer's (Lambert's) law and Beer's law. Bouguer's law states that, when a ray of monochromatic light enters an absorbing medium, its intensity decreases exponentially with an increase in the thickness of the medium traversed, or, in symbols:

$$\log \frac{I_o}{I} = Kl \qquad (2)$$

where K is a constant depending on the wavelength, the nature of the medium, and the concentration (if the medium is a solution).

Beer's law states that the intensity of a ray of monochromatic light decreases exponentially as the concentration of the absorbing material increases, or, in symbols:

$$\log \frac{I_o}{I} = K'c \qquad (3)$$

where K' is a constant depending on the wavelength, the nature of the medium, and the thickness.

The two laws may be combined thus,

$$\log \frac{I_o}{I} = kcl \qquad (4)$$

where k is now a constant depending only on the wavelength of the light and the nature of the solution. This relationship is known as the Bouguer-Beer or Lambert-Beer law.

There are no exceptions to Bouguer's law. The behavior of many substances, however, is not adequately described by Beer's law. Discrepancies are usually found when a solute ionizes, dissociates, or associates in solution. Furthermore, the relationship may not adequately describe the behavior of light which is not monochromatic. The behavior of a substance can always be tested by plotting $\log \frac{I_o}{I}$, E, or log T against the concentration. A straight line passing through the origin indicates conformity. If substances do not conform, a cali-

bration curve is best constructed for the particular determination using a series of standards of known concentration. It is also generally recommended that the concentration ranges employed not vary by a factor of more than four.

Colorimeters, or color comparators, are instruments designed to aid one to compare the intensity of color of one substance with that of a standard. In such a case, the Bouguer-Beer Law may be applied as follows:

Let the light striking each of the two solutions in Fig. I-1 be of equal intensity, I_0. Let the concentrations and depths be so adjusted that the light emerging from both solutions be of equal intensity, I. Then

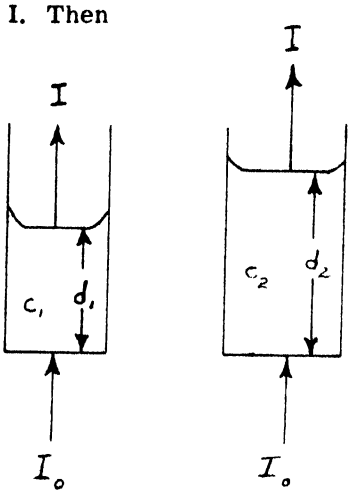

Fig. I-1. Transmission of Light Through Solutions

$$\log \frac{I_0}{I} = kc_1d_1 = kc_2d_2 \qquad (5)$$

$$c_1d_1 = c_2d_2 \qquad (6)$$

$$\frac{c_1}{c_2} = \frac{d_2}{d_1} \qquad (7)$$

This is the fundamental relationship used in color comparators.

Series of Standards and Dilution Methods. The simplest types of color comparators use a series of standard solutions of known concentrations in tubes of constant depth. The unknown solutions are compared with this series of standards. When a match is noted, the unknown obviously has the concentration of the known it matches. Such tubes are known as Nessler tubes and are made in a variety of sizes and forms (Fig. I-2).

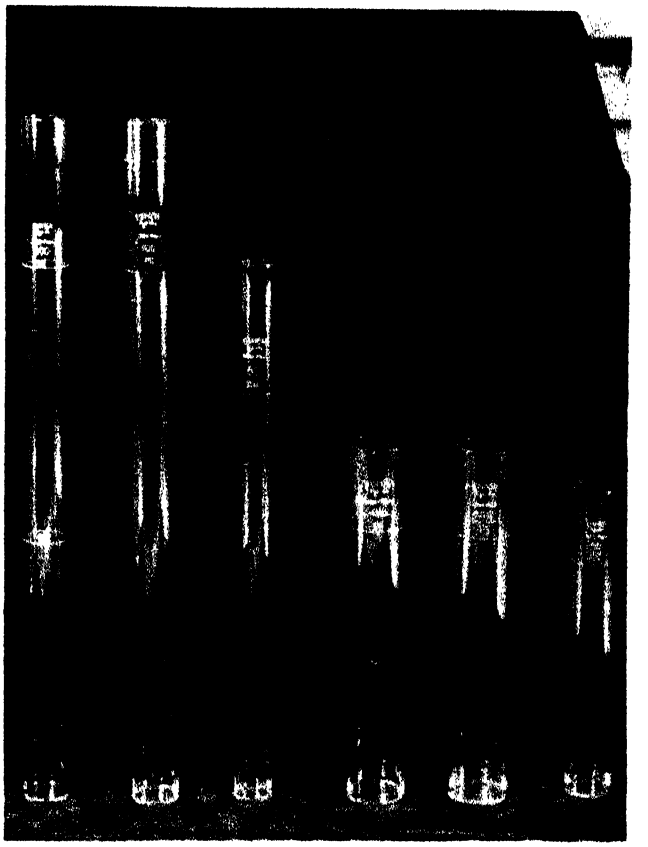

Fig. I-2. Nessler Tubes (Courtesy of Fisher Scientific Company)

The tubes may be viewed horizontally and may conveniently be held in a block or slide comparator which consists of a block or slide with vertical holes to accomodate the tubes and horizontal holes through which to view each tube (Fig. I-3). The Nessler tube method is especially valuable for weak colors, such as yellows, since a large depth can be employed.

It is generally best to match unknowns against standards of the same material similarly treated. Frequently, the colored compounds are not stable, and it may be more convenient, especially for routine work, to match the unknown with a series of permanent artificial standards. It is always most desirable to have the unknown and standard in the same physical state, but again convenience often rules in favor of solid standards.

Permanent liquid standards can frequently be prepared by mixing stable, colored, inorganic salts in the correct proportions to match each desired concentration of the unknown. Thus the color produced by chlorine and orthotolidine is

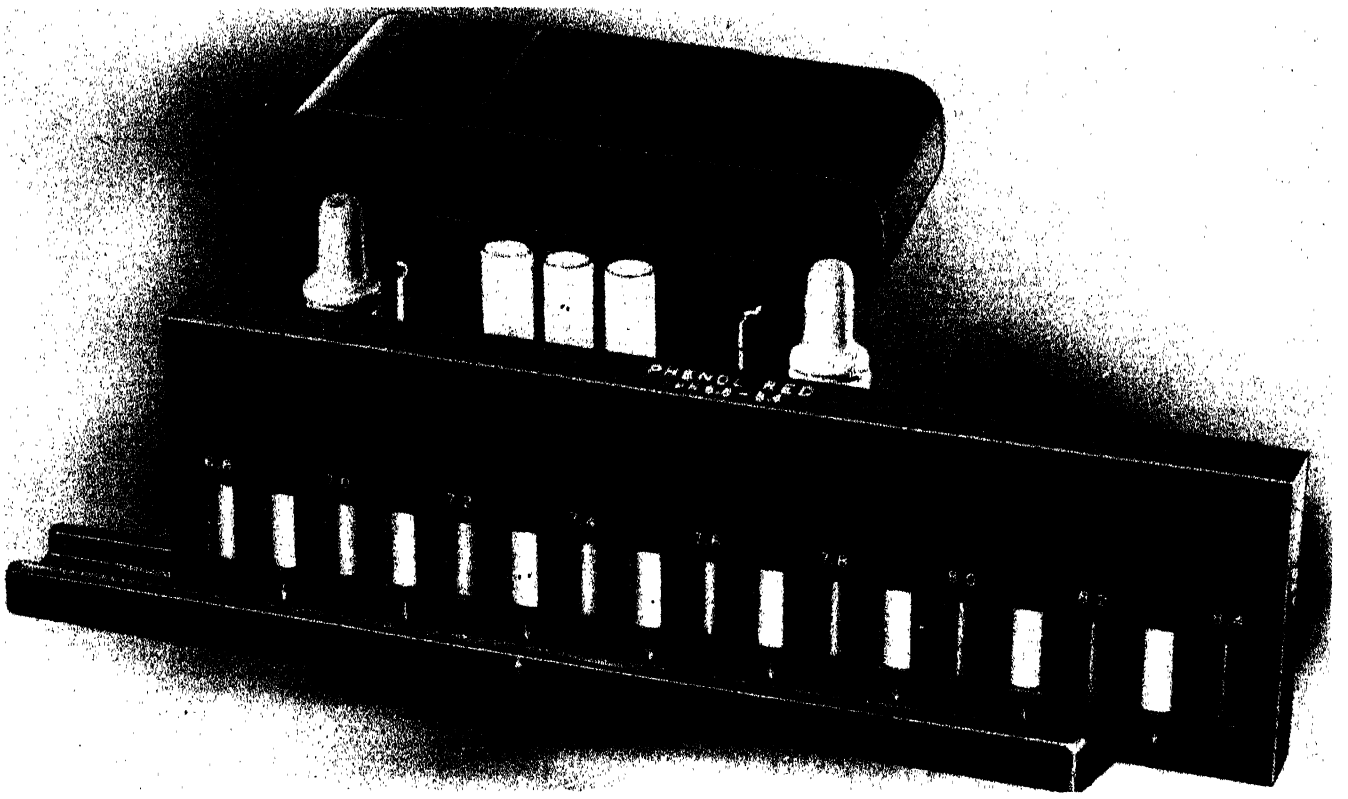

Fig. I-3. Slide Comparator, Model T-O (Courtesy W. A. Taylor & Company)

matched by mixtures of potassium dichromate and cupric sulfate. Such mixtures seldom have the same spectral absorption characteristics as the unknowns and may appear differently under different conditions of illumination. The type of illumination should, therefore, be standardized.

Solid standards may be made of various colored glasses or, for rough work, may be colored paper or cardboard charts. The Hellige comparator shown in Fig. I-4 is an example of a device using colored glass discs.

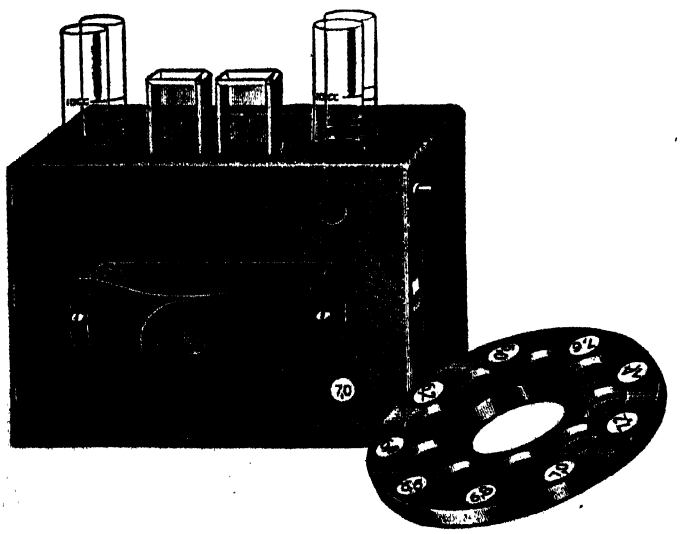

Fig. I-4. Hellige Laboratory Comparator (Courtesy of Hellige, Inc.)

Another type of color comparison, often referred to as a colorimetric titration, is based upon matching the color of the unknown solution with a known solution. The unknown is placed in a suitable container, such as a Nessler tube. To a similar tube one adds the necessary reagents and enough solvent to bring the solution almost to the level of the unknown. A standard solution of the unknown constituent is then added carefully from a buret, with constant stirring until the color almost matches that of the unknown. The solution is then diluted to the same volume as the unknown and a final match is made by adding a little standard solution from the buret. The amount of the standard constituent required is the amount of unknown contained in the volume employed in the matching process.

A similar procedure is to add solvent to one solution until, when viewed through a constant depth as through the sides of the tubes, the liquids appear to match. The solutions now have equal concentrations and the original concentrations can be calculated from the original and final volumes.

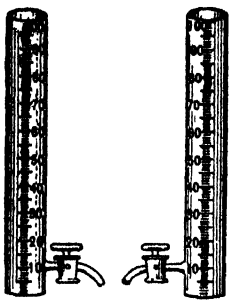

Fig. I-5. Hehner Cylinders

Variable Depth Methods. In the previously mentioned methods the solution depth has been kept constant. A match of the color intensity may be obtained by varying the depth of two solutions of different concentrations. The simplest procedure employs two graduated tubes known as Hehner tubes (Fig. I-5) with stopcocks at the sides of the base. The unknown is placed in one tube and a standard solution in the other. Liquid is drawn from the more concentrated solution, until, on looking down the tubes, the colors match. The depths are read from the graduations on the side and the concentration of the unknown is calculated by use of equation (6) or (7).

The Duboscq colorimeter shown in Fig. I-6 is probably the most widely used color comparator. A fixed, glass plunger dips into each of two solutions. The depth of solution traversed by the light beam is varied by raising or lowering the cups containing the solutions. Duboscq colorimeters are made in a wide variety of forms. Some instruments have cups to accommodate small volumes of solutions; some have scales graduated to read directly the ratio of sample to standard; some have deep cups for faint solutions; still others have water-jacketed, constant-temperature cups. The usual form of the instrument has cups which hold about 15 to 25 ml. and a millimeter scale graduated from 0 to 40 or 50 mm.

The colorimeter must first of all be kept clean. The cups and plungers are rinsed with water and either dried with a soft lens tissue or rinsed with the solution to be measured. The zero points of the scale are tested by carefully raising the cups until they touch the plungers. Most instruments have means of adjusting the zero points of the scales. Both cups are preferably filled with the standard solution and both cups are set at the same reading, say 20 mm. The light is now adjusted until it is equal on both sides. This may be accomplished by shifting the position of the instrument or mirror if daylight or an external

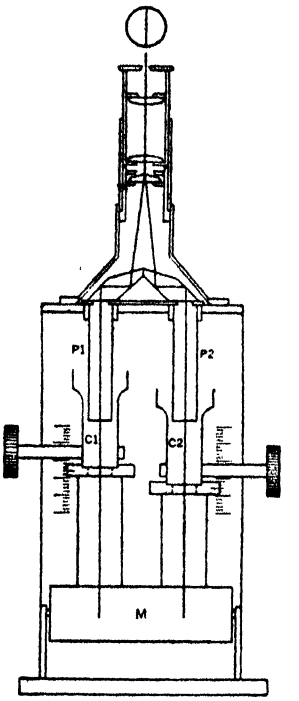

Fig. I-6. Optical Path in a colorimeter of the Duboscq Type. P_1, P_2, Plungers. C_1, C_2, Cups to hold the solutions. M, mirror. The two halves of the field viewed through the ocular appear equally bright when a match has been obtained

light source is employed, or by changing the position of the bulb or a reflector if a light source is attached to the instrument. The balance should be tested by moving one cup up and down until a match is obtained. Both sides should read the same. One solution may now be poured out and the unknown solution put in its place. Several readings are averaged together to obtain the best results. Half of the balance points should be obtained by approaching the point of balance from one direction - say, increasing the depth - and the other half from the opposite direction.

The most accurate method of using the colorimeter is to use one side as a fixed reference as follows: Fill both cups with standard solution. Adjust the light intensity as described above. Set the right-hand cup at some convenient depth, say 20 mm. Move the left-hand cup up and down to obtain a match. Average several readings of the match point. Now set the left-hand cup at this average depth. Replace the standard solution in the right-hand cup with the unknown solution and obtain several values of the match point. The left-hand cup is not disturbed. The ratio of the unknown reading to the standard reading in the

right-hand cup is used in the calculations; the left-hand cup acts only as a fixed reference point. This method of using the colorimeter eliminates slight inequalities in illumination and scale errors.

Deviations from Beer's law may be checked by diluting a sample of the solution exactly to some fraction of its original concentration, as for example to 2/3 the original concentration. The diluted solution is compared anew with the standard and should match at exactly 3/2 the depth of the original solution. In case this is not so, it is possible to use a modified form of the Bouguer-Beer relationship for the colorimeter. Yoe[2] suggests the use of the following relationship originally developed by Kober:

$$R = \frac{S}{\frac{c}{c_0}} - (1 - \frac{c}{c_0}) \frac{SK}{(\frac{c}{c_0})^2} \qquad (8)$$

where R = depth of sample solution;
S = depth of standard solution;
c = concentration of sample;
c_0 = concentration of standard;
K = constant, known as Kober's constant.

If the test of Beer's law is made as suggested above, c and c_0 refer to the original and diluted sample, and S and R to the corresponding depths. Then c and c_0 need not be known since $\frac{c}{c_0}$ is always employed and this can be calculated from the known dilution.

Beer's law is not followed exactly unless monochromatic light is employed. Furthermore, most solutions absorb in only a limited region of the visible spectrum; light of other regions passes through to the observer's eye unaltered. A filter which cuts out this unnecessary light will, then, increase the sensitivity of the method and eliminate many apparent deviations from Beer's law. In the absence of other information a filter of complementary hue to that of the solution is chosen. If the absorption curve of the material being measured is known, then a filter which transmits light of the wavelength most strongly absorbed by the solution is chosen.

The effective depth of a solution can be varied by placing the solution in a wedge-shaped cell with provision for running the cell up and down in front of a fixed opening. Such instruments are known as wedge-cell colorimeters. They are much less frequently used than are Duboscq colorimeters.

2. Yoe, J. H., "Photometric Chemical Analysis," Vol. I, John Wiley & Sons, Inc., New York, 1928, p. 75.

It has been assumed in all cases above that the original solution is colorless or that there is no color except that due to the compound being determined. It is possible to compensate for weak extraneous color of the solution. In the block comparators this is accomplished by placing two tubes, one behind the other, in each light path (Fig. I-7). Tubes A contain the weakly colored unknown solution before any additional color has been developed. Tubes B and B' consist of colored, standard solutions. Tube C contains water, and tube D contains the colored solution in which the additional color of the substance being determined has been developed. In each path there is, in effect, one tube of the weak base color and one of the developed color, and there is a total thickness of two tubes in each case. This method was suggested by Walpole.[3]

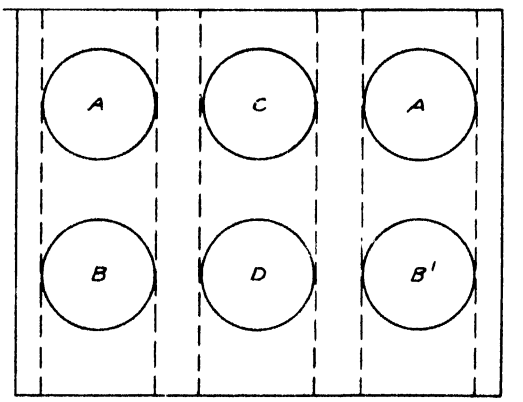

Fig. I-7. Block Comparator

Special Duboscq colorimeters are made with an extra cup of fixed depth in each light path. These cups can be used in a manner similar to that just described to compensate for weak base colors in the unknown solutions (see page 143, chapter XII).

Direct Intensity Measurements. Photometers. Rather than always to compare an unknown solution with a standard, it is possible to construct instruments which measure directly the amount of light absorbed by the solution. Such instruments are called photometers. The simplest visual photometers employ a neutral, dark glass wedge to remove light from one beam passing through the instrument (Fig. I-8). In the other beam is placed the solution being investigated. The wedge is moved back and forth until both beams are of equal intensity. The amount of light absorbed by the wedge and solution are

3. Walpole, G. S., Biochem. J., 5, 207 (1911).

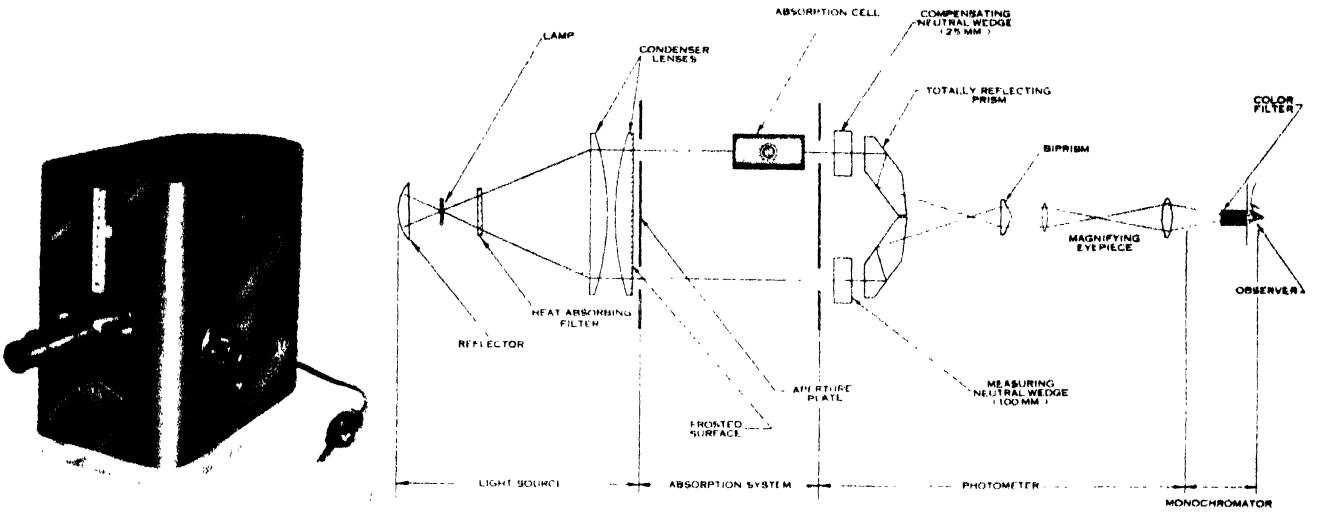

Fig. I-8. The Aminco Neutral Wedge Photometer with optical diagram (Courtesy of American Instrument Company)

now equal, and the amount absorbed by the wedge can be determined from its position (that is, thickness). Both halves of the field must be of the same hue. This is accomplished by placing filters in the light beams. Glass filters or liquid filters may be employed or, in certain special cases where the absorption maximum of the solution coincides with a bright spectral line of sodium, cadmium or mercury, a sodium, cadmium, or mercury lamp may be used with filters to remove unwanted lines. The filter should transmit as narrow a band of wavelengths as possible, yet allow sufficient light to reach the eye to insure accurate comparisons. The band transmitted by the filter should coincide with the position of maximum absorption of the sample and be centered around this point; otherwise extraneous light reaches the observer and the two halves of the field may not appear of the same hue.

In place of a neutral wedge a pair of polarizing prisms may be used to reduce the light intensity of the beam passing through the solvent layer in a photometer. Diaphragms may also be used to reduce the light intensity.

One great advantage in the use of filter instruments is that two colored constituents in one solution may be determined simultaneously provided that each does not absorb appreciably at the wavelength of maximum absorption of the other. Even when each absorbs appreciably at the wavelength of maximum absorption of the other, it is possible to set up two simultaneous equations and solve for the concentration of each substance. Thus, since extinctions or optical densities are additive,

$$(E_1)_{\lambda_1} + (E_2)_{\lambda_1} = E_{\lambda_1} \tag{9}$$

$$(E_1)_{\lambda_2} + (E_2)_{\lambda_2} = E_{\lambda_2} \tag{10}$$

where subscripts 1 and 2 refer to the two different substances and subscripts λ_1 and λ_2 refer to the two different wavelengths. E_{λ_1} and E_{λ_2} are the measured optical densities at the two wavelengths for the mixture of the two substances The wavelengths are chosen to coincide with maxima of absorption of the two substances; preferably one substance absorbs strongly and the other weakly at one wavelength and vice versa at the second wavelength.

Since $E = kc$, if the depth remains constant,

$$k_{1\lambda_1} c_1 + k_{2\lambda_2} c_2 = E_{\lambda_1} \tag{11}$$

$$k_{1\lambda_2} c_1 + k_{2\lambda_2} c_2 = E_{\lambda_2} \tag{12}$$

$$c_1 = \frac{k_{2\lambda_1} E_{\lambda_2} - k_{2\lambda_2} E_{\lambda_1}}{k_{1\lambda_2} k_{2\lambda_1} - k_{1\lambda_1} k_{2\lambda_2}} \tag{13}$$

and

$$c_2 \quad \frac{k_{1\lambda_1} E_{\lambda_2} - k_{1\lambda_2} E_{\lambda_1}}{k_{1\lambda_1} k_{2\lambda_2} - k_{2\lambda_1} k_{1\lambda_2}} \tag{14}$$

The true values of the k's can be determined from measurements on pure solutions of each substance. It is then only necessary to measure the extinction of the mixture at the two selected wavelengths in order to calculate the concentrations of the two components.

Errors. The determination of concentration of colored substances by the use of colorimeters is subject to a variety of errors. There errors may be divided into those concerned with the instrument itself; those due to the observer; and those attributable to the solution under investigation.

Instrumental errors may arise from inaccuracies in the adjustment of the illumination, errors in the calibration, and in the zero point of the scale, parallax, artificial standards, stray or reflected light entering the instrument, chipped or otherwise defective optical parts, dust on the optical parts, dirty cells, etc. It is always advisable to check the zero point of the scale. This is readily accomplished on a Duboscq colorimeter by running the cups up until they touch the plungers. The equality of illumination should be tested by placing distilled water in both cells and noting whether the fields appear the same when the plungers are at the same depth.

The eye becomes fatigued after long use so that it is recommended that a long series of observations be interrupted by frequent rest periods. The eye is more sensitive when dark adapted by remaining in a darkened room for several minutes. A colorimeter is preferably used in a darkened room or in a corner away from bright illumination. Of course, such an arrangement is impossible when daylight is used as a source of illumination. The eye is more sensitive to the green region of the spectrum than to the other regions. Yellow solutions are especially difficult to compare.

The colored compounds may not be stable. It is often necessary to specify that the comparison of two solutions be made within or during a definite period of time. It is always advisable to prepare the standards and unknowns at the same time. A turbidity in one solution will cause an error. The color of solutions may vary with temperature; thus unknowns and standards should be at the same temperature. The presence of other ions, especially colored ions, may cause appreciable errors. The standards should have the same composition as the unknowns. The use of artificial standards has been previously discussed.

LABORATORY WORK WITH THE DUBOSCQ COLORIMETER

General Instructions for the Operation of the Instrument

1. Be sure that the cups and plungers are clean before and after use. Use a soft cloth or lens tissue to wipe optical glass.
2. Test the zero of the scale by carefully raising the cups until they touch the plungers. The zero point of the scale is adjusted by screws at the bottom of the cup holders or at the side of the holders. Cups should not be changed from one side to the other.
3. Adjust the instrument for equal light intensity on both sides by filling the cups (to the shoulder, or about 3/4 full only, so as to prevent overflow when the plungers are inserted) with the standard solution; set both sides at the same value; adjust position of light until it is equal on both sides. This may be accomplished by shifting the position of the instrument or mirror if daylight or an external light source is employed, or by changing the position of the bulb or reflector if a light source is attached to the instrument, so that both sides of the field appear of equal brightness.
4. Test light adjustment by filling both cups with the standard solution and setting one cup at a convenient depth, then move the other cup until a balance is obtained. Half of the balance points should be obtained by approaching the point of balance from one direction, and the other half from the opposite direction. Repeat this balancing until about 6-10 readings have been obtained. The average of these readings should agree within 1% or 2% with the reading of the stationary cup. If this is not the case one may apply a correction factor to each reading or, better still, use one side as a fixed reference as follows: Set the cup just moved (cup 2) at the average reading obtained for it. Leave the standard solution in this cup (cup 2). Replace standard solution in the other cup (cup 1) with the unknown solution. Adjust the unknown cup (cup 1) until a balance is obtained. Then

$$C_{unknown} = C_{standard} \times \frac{R_{standard}}{R_{unknown}}$$

where

$R_{standard}$ = reading of standard solution in cup 1;

$R_{unknown}$ = reading of unknown in cup 1.

5. Be sure that there are no air bubbles beneath the plungers when the plungers are inserted beneath the liquid.

Preparation of Solutions for Phosphate Determination

This is a simplified Fiske-Subbarow method.[4] The unknown consists of a solution of a phosphate in the same concentration of sulfuric acid as in the standard solution. The phosphate is first converted to the complex molybdiphosphate ion by adding excess molybdate ion. The molybdenum in the complex ion is easier to reduce to a blue-colored, lower-valence form than the molybdenum in the simple ion. Selective reduction of the complex ion is accomplished by the mild reducing agent, 1-amino-2-naphthol-4-sulfonic acid.

Solutions Required. 1-amino-2-naphthol-4-sulfonic acid 0.25% solution. Dissolve 0.5 g. dry powder in 195 ml. of 15% sodium bisulfite and 5 ml. of 20% sodium sulfite.

Molybdate solution. Dissolve 25 g. of ammonium molybdate in 200 ml. of water, rinse into a 1 liter volumetric flask containing 500 ml. of 10 N sulfuric acid. Dilute to the mark and mix.

Standard phosphate solution. Dissolve 0.3510 g. of potassium dihydrogen phosphate in water, add 10 ml. of 10 N sulfuric acid, dilute to 1 liter, and mix. Each ml. contains 0.00008 g. of phosphorus.

Method. Pipet 10 ml. of standard phosphate solution or unknown solution into a 25 ml. volumetric flask. Add 2 ml. of 2.5% molybdate solution and 0.8 ml. of 1-amino-2-naphthol-4-sulfonic acid 0.25% solution. Dilute to the mark with distilled water, mix, let stand 5 minutes, and compare in the colorimeter.

Calculate the mg. of P per ml. of unknown solution. Report this value, with the readings, etc. in a suitable notebook.

Preparation of Solutions for Ammonium Ion Determination Using Nessler's Reagent. Nessler's reagent is an alkaline solution of potassium mercuric iodide which reacts with ammonia to form an orange-colored complex, probably a colloidal solution, of $HgO.Hg(NH_2)I$.

4. Fiske, C. H. and Subbarow, Y., J. Biol. Chem., 66, 375 (1925).

Solutions Required. Standard Ammonium Sulfate. Dissolve 0.4715 g. of ammonium sulfate in water and dilute to 2 liters.

Sodium hydroxide, 10%. Dissolve 100 g. of sodium hydroxide in 1 liter of water with cooling.

Nessler's reagent. Dissolve 2.5 g. of potassium iodide in 3 ml. of water, add 3.5 g. of mercuric iodide, and stir until solution is complete. Then add 100 g. of a 15% solution of potassium hydroxide, mix, allow to settle, and decant the clear supernatant liquid. Keep the solution in the dark.

Method. Transfer 10.00 ml. of standard ammonium sulfate solution (1ml. contains 0.05 mg. of N) into a clean 100 ml. volumetric flask. Add 1 ml. of 10% sodium hydroxide solution. Dilute to about 75 ml. and shake. Pour into a graduated cylinder 10 ml. of alkaline Nessler's reagent. Swirl the volumetric flask (to set the solution spinning within the flask) and rapidly add the Nessler's reagent. A deep red but crystal clear solution should result. If not, discard and prepare a fresh standard.

Prepare the unknown solution in the same manner using 10.00 ml. of the unknown solution in place of the standard ammonium sulfate solution.

Dilute the contents of both flasks to 100 ml., stopper, and shake. Compare in the colorimeter.

Calculate the milligrams of nitrogen per milliliter of unknown solution.

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CHAPTER II

PHOTOELECTRIC COLORIMETERS AND FLUORESCENCE METERS MEASUREMENT OF RADIANT ENERGY

One of the greatest improvements in the design of colorimeters has been the use of photoelectric cells or thermocouples to measure the intensity of the light. Thus errors due to the personal characteristics of each observer have been largely eliminated. Before describing the types of instruments available, it is necessary to review the characteristics of the light sensitive devices employed. Barrier layer and photoemissive type cells are most commonly employed, but thermocouples and photoconductive cells have been used. Although bolometers and thermistors are not commonly used in the visual and ultraviolet regions they will be considered here because they are widely used in the infrared regions.

Photoemissive Cells. Photoemissive cells are of two main types - high vacuum and gas filled. In both types the sensitive surface is usually a metal plate covered with a composite coating. The Ag-O-Cs type cathode surface is made in the following manner. A silver-plated nickel sheet is carefully oxidized to silver oxide in an oxygen atmosphere by means of a glow discharge, then a layer of cesium metal is distilled onto the silver-silver oxide surface, and finally the tube is subjected to a baking process which results in the formation of some cesium oxide on the surface through interaction of cesium with the silver oxide layer. Such composite coatings are as much as one thousand times as sensitive as the bulk metal alone.

Regardless of the composition of the cathode surface, the following conditions must be adhered to if a sensitive surface is to result. (1) An adequate absorption of light must occur, that is, the surface must not be transparent nor highly reflective. (2) An element must be used that has low atomic binding forces, such as the alkali metals which will easily part with their outer electron due to their low ionization energy, E_i. (3) The surface layers through which the electrons must travel before escaping must possess small forces of attraction for the electrons, that is, low work function, φ. (4) The specific resistance of the cathode must approximate that of a semiconductor, since metallic conductors are too reflective and insulators prevent the replacement of electrons released by light.

Table 1

Ionization Energy, E_i, and Work Function, φ, of Some Chemical Elements

	E_i	φ
Na	5.1	2.5
K	4.3	2.3
Rb	4.2	2.1
Cs	3.9	1.8

Equation (1) expresses the relationship between the wavelength, λ, of the incident light necessary to cause a photocurrent to flow and the work function, φ. V is the velocity of the emitted electrons expressed in volts; and h, Planck's constant; c, the velocity of light (in cm./sec.); and e, the electronic charge (in e.s.u.), are universal constants.

$$V = \frac{hc}{e\lambda} - \varphi = \frac{12{,}400}{\lambda} - \varphi \qquad (1)$$

For the minimum velocity of an electron barely able to escape from the surface layer, the maximum wavelength, or threshold wavelength, λ_o, which will barely release a photoelectron from a surface whose work function is φ, is given by equation (2).

$$\lambda_o = \frac{12{,}400}{\varphi} \quad \text{when } V = O \qquad (2)$$

Photoemissive tubes will not respond, therefore, to wavelengths in the infrared longer than about 12,000 Å.

The difference in potential maintained between the two electrodes of the phototube is important. If the potential is not high enough, all electrons ejected from the cathode may not reach the anode. Above a certain potential, all electrons will be attracted to the anode and a saturation photoelectric current is said to be obtained. The necessary potential increases with an increase in light intensity and thus an increase in numbers of electrons emitted. Typical curves showing the relationship between photoelectric current and applied potential for a high-vacuum photocell are shown in Fig. II-1, and the linear relationship between saturation photoelectric current and

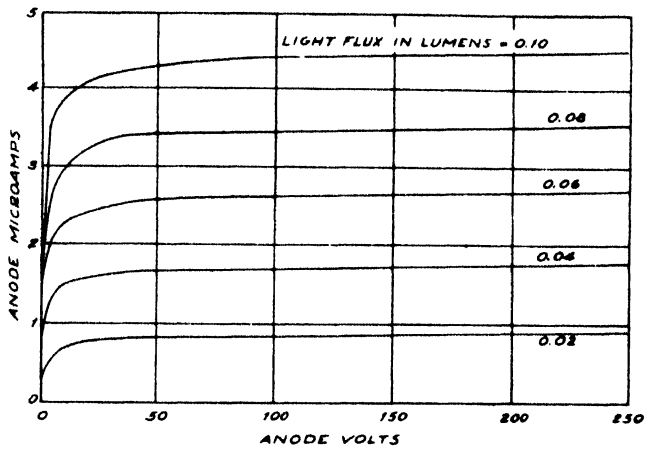


Fig. II-1. Typical anode characteristics of high vacuum phototube (R.C.A. 929)

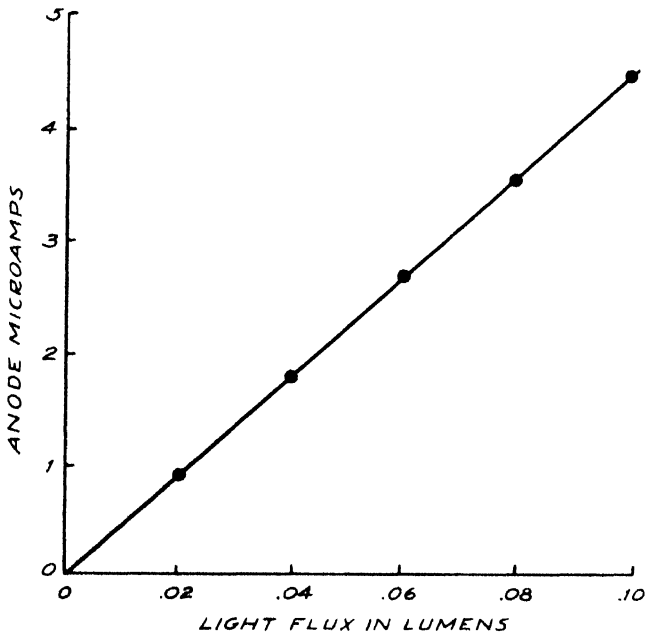


Fig. II-2. Relationship between light intensity and saturation photocurrent for a typical high vacuum phototube (R.C.A. 929)

intensity of illumination is shown in Fig. II-2. Strict proportionality between photocurrent and light intensity is a fundamental law of photoelectricity, but its realization in practice demands a carefully designed and constructed cell. The color sensitivity of a cell can be varied by using different alkali metals and by variations in the method of preparation. The response of commercial type cells is shown in Fig. II-3.

A gas-filled photocell generally contains argon at about 0.2 mm. pressure. As the electrons

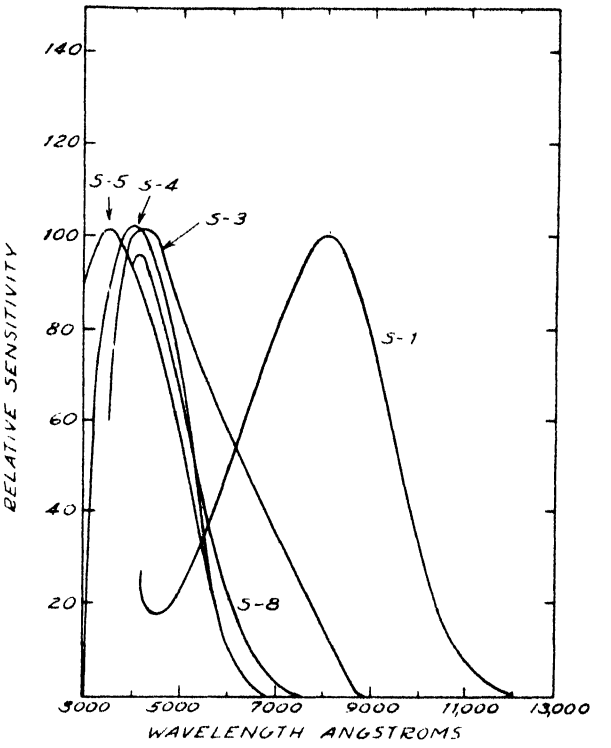


Fig. II-3. Spectral response of commercial phototubes

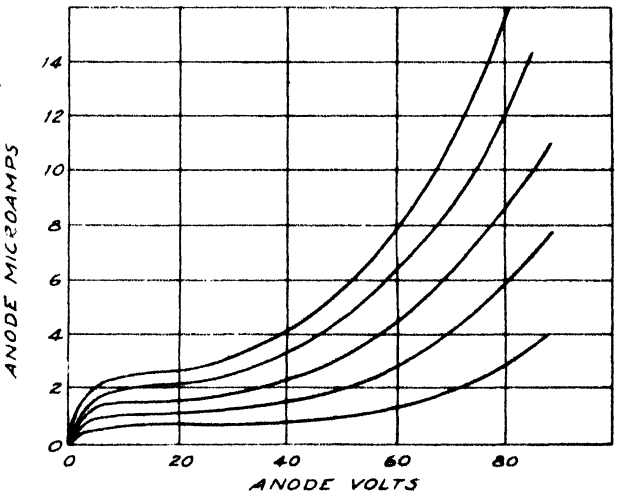


Fig. II-4. Typical anode characteristics of gas-filled phototubes (R.C.A. 930)

travel toward the anode they may collide with the gas molecules and, if the electrons possess sufficient energy, the gas molecules will be ionized. These ions enhance the current, and the primary photocurrent may be increased tenfold. The relationship between applied potential and photoelectric current is shown in Fig. II-4. Gas-

filled cells are not used very much in instrumental construction because they do not show a linear response to light intensity except at very low voltages where the electrons do not have sufficient energy to ionize the gas. Thus no advantage is obtained by the presence of the gas. The cells also show a time lag and begin to show a drop in sensitivity to modulated light sources with frequencies above a few hundred cycles per second.

A great magnification of primary photocurrent may be obtained with the retention of linear response by the use of the so-called photomultiplier tube. This tube is constructed (see Fig. II-5) so

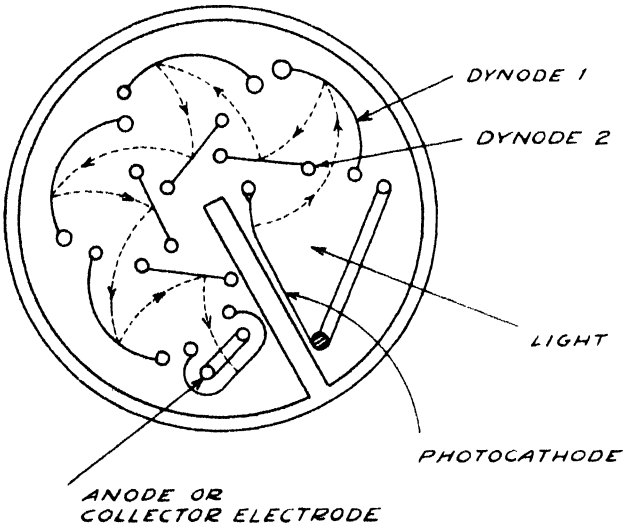


Fig. II-5. Schematic diagram of a photomultiplier tube. Dotted lines are the paths traveled by the secondary electrons as they are focused by each succeeding dynodes field in turn

that the primary electrons are attracted to dynode number 1, consisting of a plate of material which ejects several electrons when struck by one oncoming electron. These secondary electrons are directed to dynode number 2 by an additional positive potential and so on through nine stages. The final current produced may be 10^6 times the primary current. The successive stages are operated at voltages increasing in equal steps of about 50 to 100 volts. The limit of amplification is determined by two factors - noise level (random voltages) and leakage current. The ratio of the multiplier tube over the ordinary vacuum cell in the former respect is about one thousand fold, and the superiority increases as the illumination decreases. Since the output current should not exceed a few milliamperes, the use of the tube is limited to low light intensities. Leakage current, however, limits the sensitivity to about 10^{-12} amperes of photo-

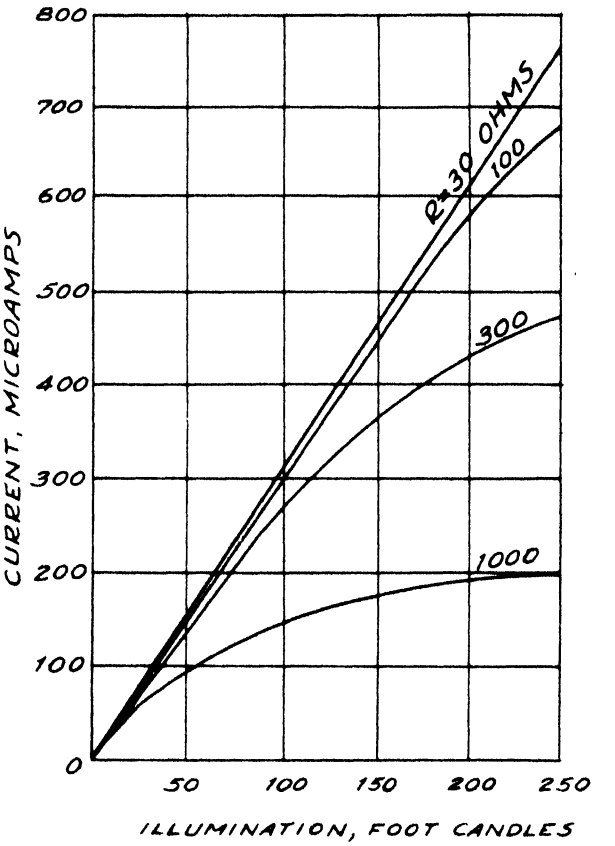


Fig. II-6. Relationship between illumination and output for a typical barrier-layer cell

current. Even in the limiting case the multiplier is capable of detecting and measuring illumination about 200 times weaker than the ordinary photocell and amplifier.

Barrier Layer Cells. A barrier layer cell, also known as a photovoltaic or blocking layer cell, consists of a plate of metal, usually copper or iron, upon which has been deposited a layer of selenium. Cuprous oxide is sometimes used in place of selenium. A very thin grid or layer of a good conducting metal is placed over the selenium layer to act as an electrode. The metal plate acts as the second electrode. When light falls upon the selenium surface through the grid a potential is developed. If the resistance in the external circuit is small, that is, about 100 ohms or less, the current produced by such a cell is very nearly proportional to the intensity of illumination as shown in Fig. II-6. The open circuit potential developed is nearly proportional to log I (see Fig. II-7). Barrier layer cells respond from the X-ray region up to around 10,000 or 12,000 Å.

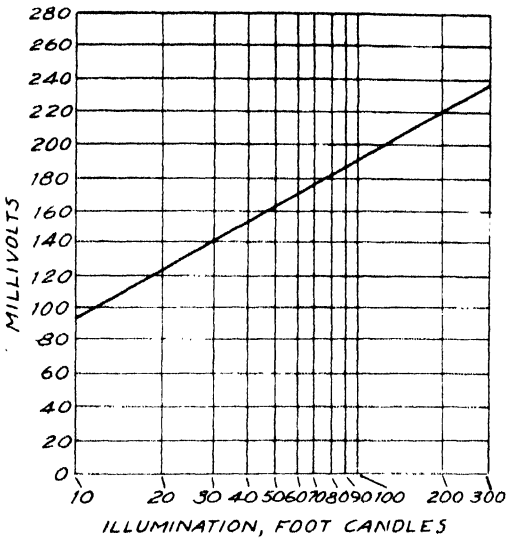


Fig. II-7. Relationship between open circuit potential and illumination for a barrier-layer cell

As compared to photoemissive tubes, barrier layer cells are much more rugged and may produce currents as high as 120 microamperes per lumen. The best high vacuum cells, except the multiplier cells, produce currents of the order of 40 to 60 microamperes per lumen. Because of the low internal resistance of barrier layer cells, the current produced cannot be readily amplified, and, therefore, they are principally used where low cost, portability, and ruggedness are demanded. On the other hand, photoemissive cells have very high internal resistances and are readily amplified. Thus the latter cells are usually employed in the most sensitive devices measuring low intensities of light. Photoemissive cells may be ruined by strong light, however.

Barrier layer cells show fatigue effects, that is, upon illumination the photocurrent rapidly rises to a value several per cent above the apparent equilibrium value and then falls off gradually. The effect is more pronounced at high levels of illumination. Recovery of the original sensitivity occurs on standing in the dark.

Thermocouples. A thermocouple consists of wires of two different metals, joined together at their ends. If one junction is at a higher temperature than the other, a potential is produced and a small current flows. Since the radiant energy must first be converted to heat energy, the "hot" junctions are generally covered with some black material. The thermocouple is most useful for regions of long wavelength, that is, the infrared region, where the transformation of radiant energy to heat is easy. The thermocouple has a low internal resistance and direct amplification of the potential produced is, accordingly, difficult.

Thermocouples are commonly constructed from the following pairs of metals or alloys: Cu - constantan; Fe - constantan; Bi--Bi + Sn alloy, Pt--Pt + Rh alloy.

Bolometers. The increase in resistance of a metal as the temperature is increased is usually of the order of 0.4% per ^{o}C. If two thin platinum foils are used as two of the arms in a Wheatstone bridge circuit and the bridge is balanced, then when light is allowed to fall on one of the platinum foils the bridge will become unbalanced due to the increase in temperature and the corresponding increase in resistance of the illuminated arm. Such a device, known as a bolometer, obviously can be used to determine the intensity of illumination. Like the thermocouple, the bolometer is most widely used in the infrared region where the radiant energy is easily converted to heat. Since the resistances involved are low, direct amplification is difficult. However, by using pulsating light sources a pulsating off-balance current can be produced. This current can be amplified with an alternating current amplifier. Similar schemes can be worked out for thermocouples and thermistors.

Thermistors. A thermistor is a substance, usually a fused mixture of oxides of copper, cobalt, manganese, nickel, and other metals, which shows a negative thermal coefficient of electrical resistance. This coefficient is approximately 4% per degree and, since this is about ten times the coefficient (but of opposite sign) for metals, the thermistor is a sensitive device for determining changes in temperature. The resistance of the device is the property measured. Two thermistors may be connected in a Wheatstone bridge circuit in much the same manner as a bolometer. Like the bolometer, the thermistor is most widely used for infrared work where the radiant energy is easily converted to heat energy. Thermistors are available in a wide variety of shapes and forms.

Thermistors, bolometers, and thermocouples are usually enclosed in a highly evacuated bulb in order to minimize fluctuations in temperature caused by conduction, by pressure changes, etc.

Light Sources. A brief consideration of the light sources which have been found most useful in photoelectric work will be helpful at this point. The most common source in the visible and the near ultraviolet and infrared regions is the ordinary tungsten filament, incandescent lamp. The

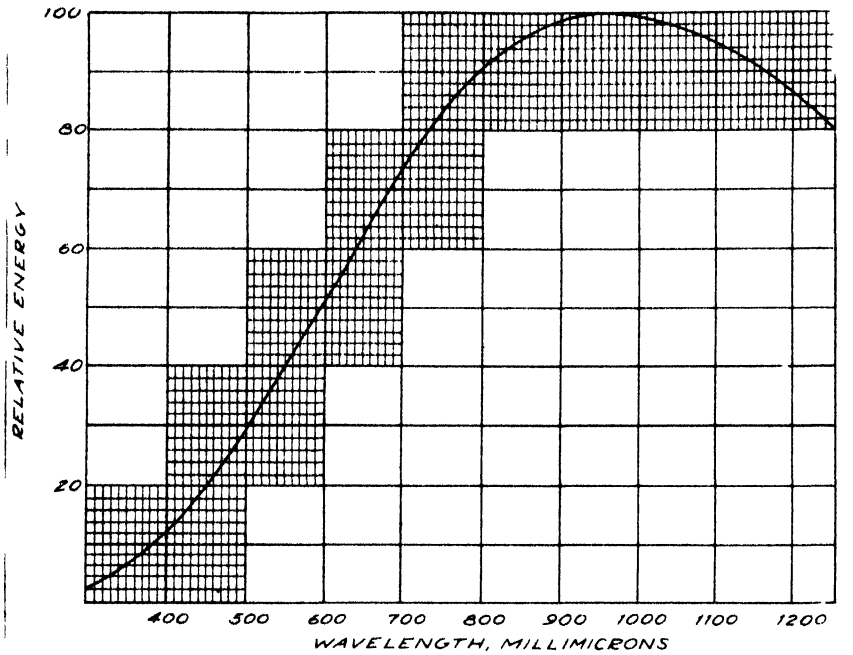


Fig. II-8. Relative energy distribution of tungsten lamp at color temperature of 2870°K

operating temperature is frequently about 2870° K. Such a lamp emits a very considerable portion of its energy in the infrared region of the spectrum (see Fig. II-8). An increase in the temperature of operation of the lamp increases the total energy output and decreases the wavelength of the maximum of the energy versus wavelength curve, but it also shortens the life of the lamp. Lamps larger than necessary are often built into equipment and run at lower voltages in order to increase the life of the lamp.

In general, if a photocell is illuminated with the total radiation from a lamp, the photocurrent, i, can be expressed as a function of the voltage, V, applied across the lamp terminals by the equation

$$i = KV^n \qquad (3)$$

The exponent, n, has a value between 3 and 4 for an incandescent lamp. This means that, if it is desired to reproduce the photocurrent to within 1%, which is average photometric precision, the lamp voltage must not vary more than a few tenths or hundredths of a volt. Such a lamp is frequently operated from storage batteries to attain the desired voltage regulation or, if operated from the A.C. mains, is carefully regulated by constant voltage transformers or electronic voltage regulators. Obviously, it is preferable to cancel out the effect of variations in light intensity by devising an instrument with two cells, one acting as a standard and one the measuring cell, with suitably designed amplifiers or measuring circuits which eliminate the effect of variation in the intensity of illumination. Measuring circuits are considered later.

In the ultraviolet region, the best source of continuous radiation is the hydrogen discharge tube. Such tubes are available in two types, those employing a high voltage and those employing a low voltage with the additional aid of a heated cathode, The Beckman Spectrophotometer employs a low voltage, heated cathode type.

When very high levels of illumination are desired, as in many fluorescence meters, mercury vapor lamps may be employed. Such lamps as the General Electric H-4 type emit a large amount of continuous radiation plus some more intense radiation in the wavelengths characteristic of the mercury spectrum. The lamps are useful in the visible and the near ultraviolet regions of the spectrum, the lower limit being usually determined by the type of glass used for the envelope. Since the lamps become very hot in operation, they must be well insulated thermally from the rest of the instrument and are often cooled by a fan during operation. The lamps of the H type increase rapidly in intensity for about 15 minutes after starting, so sufficient time should be allowed after starting the lamp to ensure substantial constancy.

Globars and Nernst glowers are popular sources of infrared radiation since they can be operated in air without an envelope. The Globar is a rod of silicon carbide heated to a high temperature by the passage through it of a consider-

able current, usually 5 to 6 amperes at about 50 volts. The Nernst glower is a small rod of refractory oxides which, when once heated, will conduct the electric current and thus maintain the high temperature required for the emission of large amounts of infrared radiation. The glower is frequently started by placing next to it a platinum wound heater which can be shut off by a relay when the glower itself becomes hot enough to conduct electricity. In the wavelength region around 3 μ, the Nernst glower has somewhat of an advantage in the amount of radiation emitted. Above 3 μ the advantage is a little in favor of the Globar, especially because it has a high heat capacity compared to the Nernst glower and is, on that account, a little steadier.

Amplifiers and Measuring Circuits. Instruments employing barrier layer cells and high levels of illumination may use sensitive galvanometers or microammeters directly to measure the output of the cells. When two cells are used and a comparison between the output of the two cells is desired, the following measuring circuits are often employed.[1] (Figs. II-9 to II-11).

It should be emphasized at this point that not all measuring circuits will automatically compensate for variations in the intensity of the light source even though two cells may be employed. This can be proved by employing Kirchhoff's laws to calculate the current flowing through the galvanometer circuit just as balance is being attained and then differentiating the current with respect to light intensity. This differential, when set equal to zero, will show the conditions wherein the fluctuations in intensity of illumination do not affect the galvanometer reading or balance point. Thus for the circuit shown in Fig. II-9:

$$i_g = i_2 - i_1 \qquad (4)$$

where i_g = galvanometer current;

i_1 = current in working cell circuit;

i_2 = current in reference cell circuit.

Now, if the cells show linear response.

$$i_1 = kTI \text{ and } i_2 = kI \qquad (5)$$

where T = transmittancy of solution;

I = intensity of illumination.

1. See Müller, R. H., Ind. Eng. Chem., Anal. Ed., 11, 1 (1939).

$$\text{Thus, } i_g = kI - kTI \qquad (6)$$

$$= kI(1-T) \qquad (7)$$

$$\frac{di_g}{dI} = k(1-T) \qquad (8)$$

$$\frac{di_g}{dI} = 0 \text{ when } T = 1 \qquad (9)$$

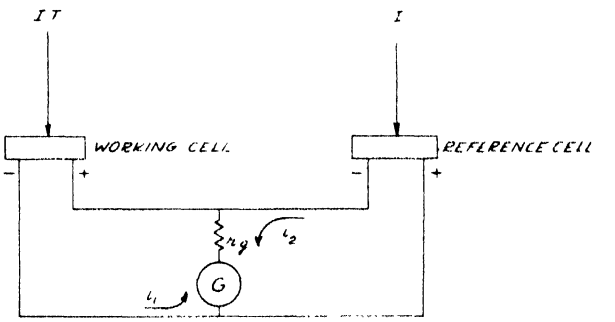


Fig. II-9. Barrier layer cells in opposition

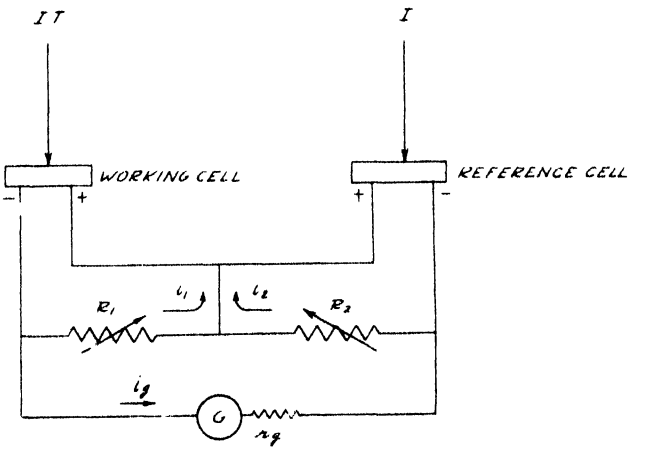


Fig. II-10. Barrier layer cells in a bridge circuit.

Therefore this circuit will compensate for variations in illumination only when the sample does not absorb - a rather useless case. On the other hand, similar analysis of the circuit shown in Fig. II-10 shows:

$$i_g r_g + (i_2 + i_g)R_2 + (i_g - i_1)R_1 = 0 \qquad (10)$$

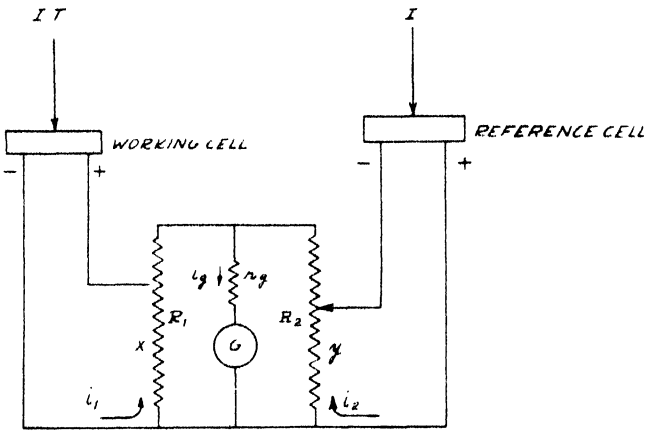


Fig. II-11. Barrier layer cells in a bridge-potentiometer circuit

$$\frac{di_g}{dI} = 0 \text{ when } R_2 = TR_1 \qquad (13)$$

and since the condition for balance of this circuit is $\frac{R_2}{R_1} = T$, the circuit is insensitive to variations in intensity of illumination when it is balanced - a very useful situation.

Amplifiers and measuring circuits for photoemissive tubes are much more complicated. A simple circuit[2] is shown in Fig. II-12.

The amplifier tube shown may be a 6H5, 6C5,

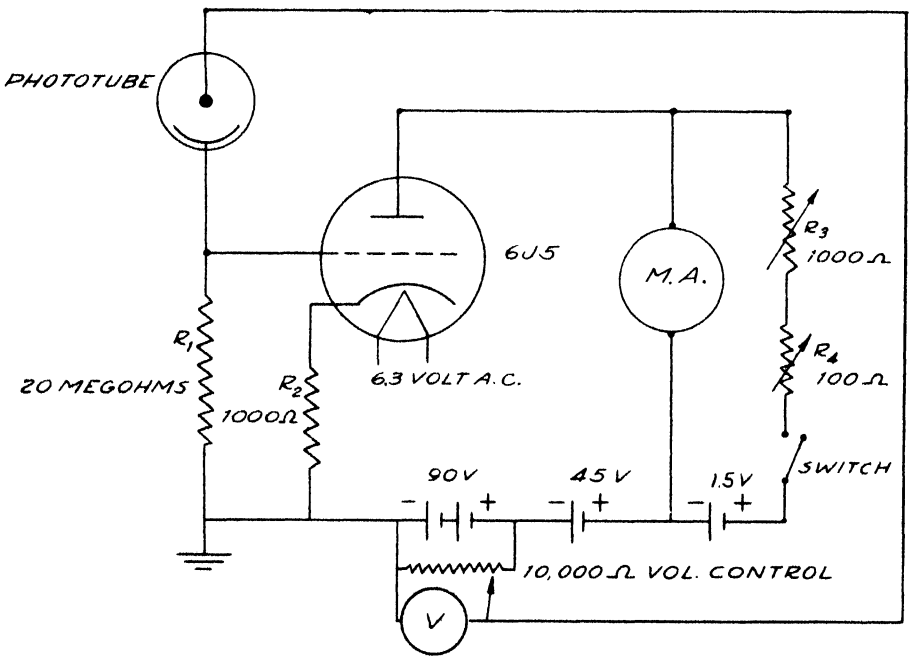


Fig. II-12. Simple laboratory amplifier circuit

$$i_g = \frac{kIR_2 - kTIR_1}{r_g + R_1 + R_2} \qquad (11)$$

$$\frac{di_g}{dI} = \frac{kR_2 - kTR_1}{r_g + R_1 + R_2} \qquad (12)$$

6F5, 6K5, 6SF5, 7A4, 7B4, or similar triode. The grid and plate potentials are adjusted to the rated values for the particular tube chosen. The

2. Müller, R. H., Garman, R. L. and Droz, M. E., "Experimental Electronics," Prentice-Hall, Inc., New York, 1945, p. 54.

photocell battery provides a potential high enough to produce saturation currents in the phototube at the usual light intensities. Upon illumination the phototube produces a current, i, which flows through the high resistance, R_1, thereby producing a potential difference E_g across its terminals. This will make the grid more positive with respect to the cathode and consequently the plate current will be increased by an amount ΔI_p. The relationship between grid potential and plate current for a typical triode is shown in Fig. II-13. The magnitude of the change in plate current, ΔI_p, is governed by the grid-plate transconductance, G_m, of the amplifier tube. The transconductance is defined by the equation

$$G_m = \left(\frac{\partial I_p}{\partial E_g} \right)_{E_p} \qquad (14)$$

where E_p is the plate potential. For any particular tube the value of the transconductance depends on the grid and plate potentials. The value for the circuit of Fig. II-12 is 3000 micromhos. This means that a change in E_g of 1 volt would produce a change in plate current of 3 milliamperes. If R_1 is equal to 20 megohms, then a photocurrent of 1×10^{-8} amperes would produce a change of plate current of 0.6 milliamperes, a gain of 60,000 fold. This is a very conservative case and by no means approaches the limit to which this process of amplification can be extended.

Since the negative grid bias voltage (with respect to the cathode) is obtained from the cathode resistor, R_2, as in inverse feed-back circuits,

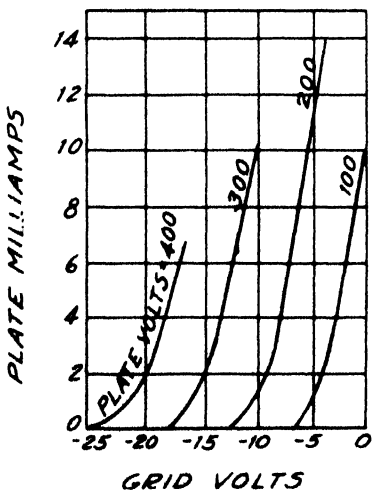


Fig. II-13. Relationship between grid potential and plate current for a typical triode (R.C.A. 655)

the output current will be almost linear with respect to input voltage. The initial plate current, which flows even with the photocell in the dark, may be balanced out with the aid of an auxiliary battery and the resistors R_3 and R_4. The sensitivity of the whole unit may be regulated within limits by changing the value of R_1.

The extent of amplification by a single-stage process is limited by several factors which build up the so-called background noise level, that is, by grid currents, insulation leakage currents, ionization currents within the triode, photoelectrons, and soft X-rays emitted from the tube elements. Furthermore, the iR_1 drop must not be so large that the potential across the photocell is reduced to a value below the saturation voltage.

Instruments. The actual photoelectric filter photometers or colorimeters may be first divided into two main classes; One-cell and two-cell instruments. Examples of the design of one-cell instruments are the Evelyn Photoelectric Colorimeter shown in Fig. II-14 and the Cenco-Sheard Photelometer shown in Fig. II-15. When using one-cell instruments, it is necessary to maintain a constant light source while the pure solvent

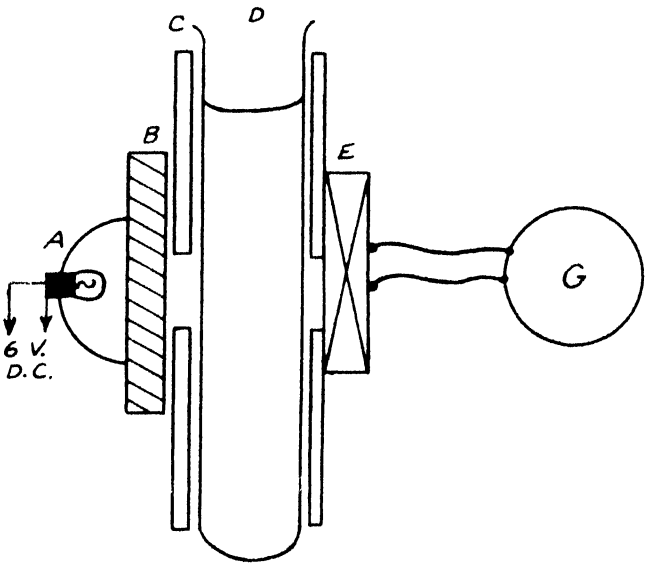
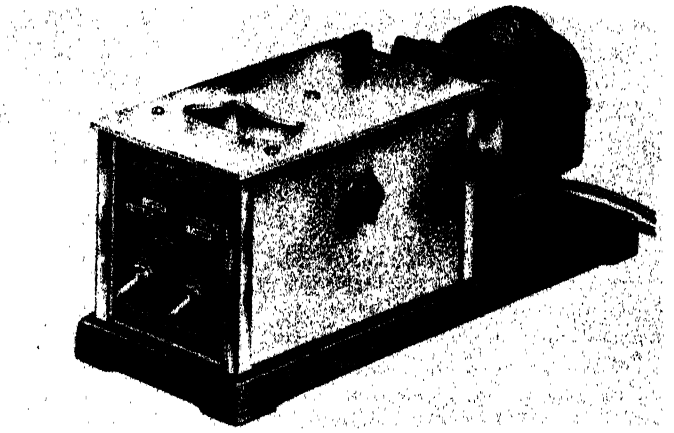


Fig. II-14. Schematic diagram of Evelyn Photoelectric Colorimeter

A - Light source and reflector
B - Filter
C - Holder for test tubes
D - Test tube containing sample
E - Barrier layer cell
F - Galvanometer



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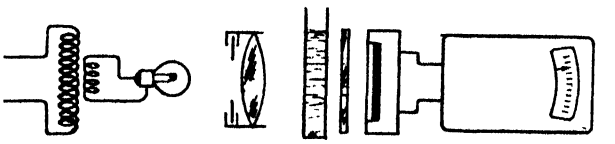


Schematic diagram of the "Photelometer". The parts are: T-Constant Wattage Transformer; S-Light Source; I-Iris Diaphragm; L-Lens; A-Absorption Cell; F-Light Filter; P-Photoelectric Cell; and M-Microammeter

B

Fig. II-15. Cenco-Sheard-Sanford Photelometer (Courtesy of Central Scientific Co.)

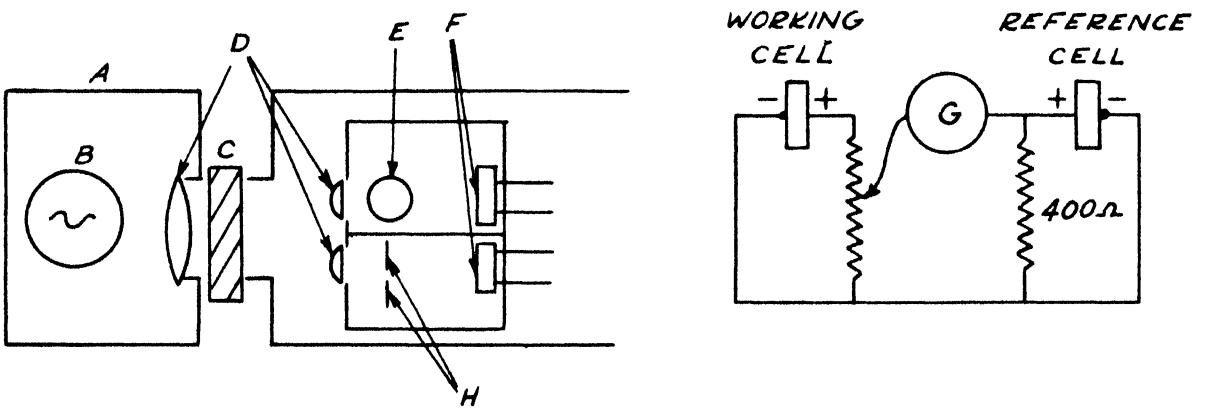


Fig. II-16. Schematic and wiring diagram of Klett-Summerson Photoelectric Colorimeter

A - Lamp Housing
B - Lamp
C - Filter
D - Lenses
E - Test Tubes
F - Barrier Layer Cells
G - Galvanometer
H - Adjustable Shutter

readings and the standard or unknown solution readings are being taken.

There are two different types of two-cell instruments - the optically compensated type and the potentiometric type. In the optically compensated type, the intensity of the light striking the reference photocell is decreased by a diaphragm or other device until it matches the intensity of the light passing through the solution. These instruments can employ photocells which do not respond linearly with intensity of illumination. The most popular of the filter photometers are the two-cell instruments of the potentiometer type. Typical examples of commercially available instruments are the Klett-Summerson, Figs. II-16 and II-17, the Lumetron Photoelectric Colorimeter, Fig. II-18, and the Fisher Electrophotometer, Fig. II-19. If the potentiometer circuits are properly chosen, variations in light intensity are canceled out. The dials on such instruments may be calibrated in per cent transmittancy or in extinction (optical density), or both. If the readings are in per cent transmittancy, it is convenient to plot reading versus concentration on semi-logarithmic paper in order to obtain straight lines. A plot of log per cent transmittancy or of extinction versus concentration gives a straight line directly, provided always, of course, that the colored substance obeys Beer's law.

Errors in the use of photoelectric colorimeters may arise from a number of sources. Some significant instrumental errors which may occur are the following:

1. Nonlinearity of response of the light sensitive devices and the associated measuring cir-

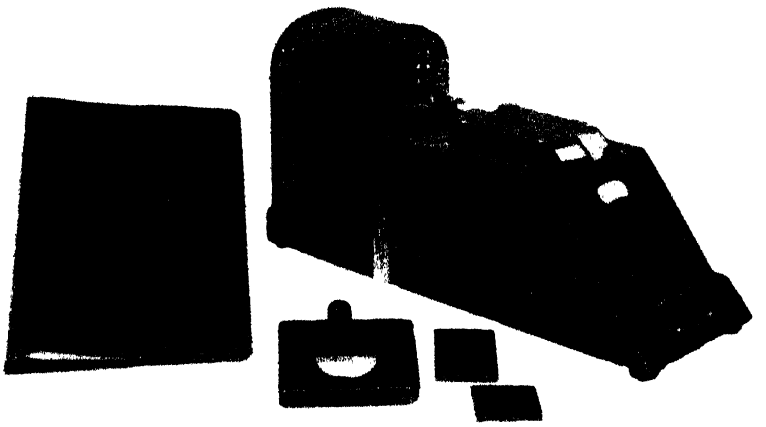


Fig. II-17. Klett-Summerson Photoelectric Colorimeter (Courtesy of Klett Manufacturing Co.)

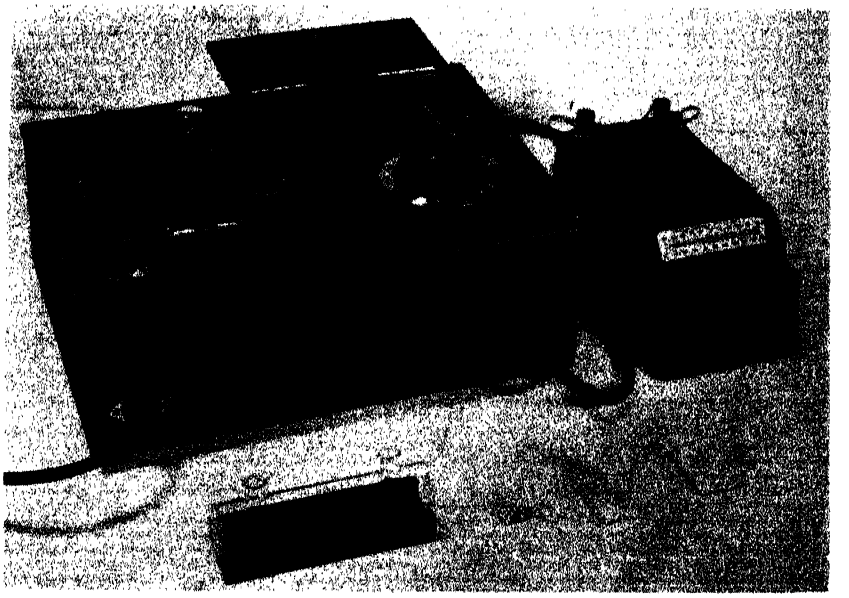


Fig. II-18. Lumetron Photoelectric Colorimeter (Courtesy of Photovolt Corp.)

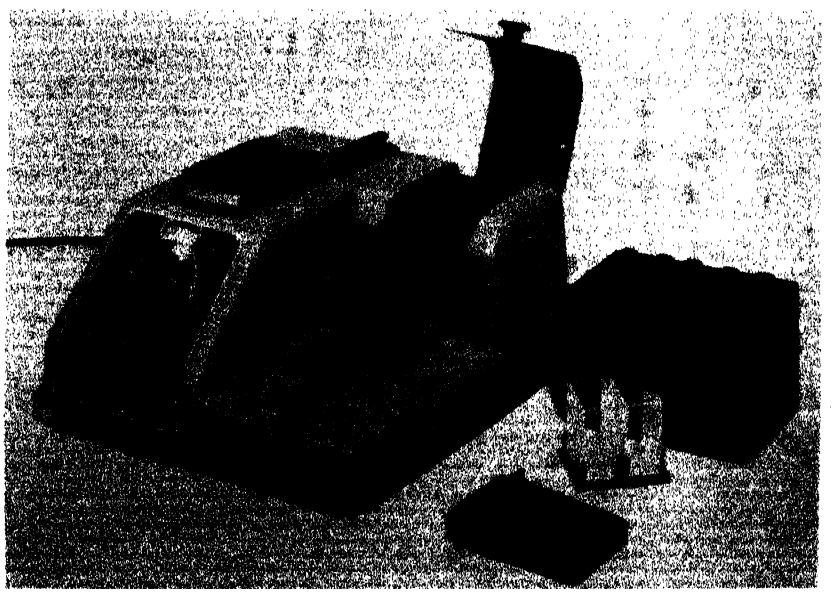


Fig. II-19. Fisher Electrophotometer (Courtesy of Fisher Scientific Co.)

cuits. These errors can be avoided by careful selection and matching of photocells and by careful design of the amplifying or measuring circuits.

2. Variations in intensity of the light source. Such variations can be eliminated by properly designed two-cell instruments and can be controlled by careful regulation of the voltage applied to the source in other instruments. Rapid exchange of solvent and solution cells is recommended on one-cell instruments. The solvent should be replaced and the original reading rechecked.

3. Stray light striking the cells may be a serious source of error. Such light can usually be eliminated by properly placed baffles and light tunnels in the instrument. Removing extraneous light by use of the proper filters also helps.

4. A rise in temperature of the measuring photocells may cause error. This can be partially eliminated by using heat absorbing filters in the optical system, by choosing similar photocells in two-cell instruments, and by proper thermal insulation of the light source from the rest of the instrument.

5. Dust, scratches, and imperfections in the optical system. Extreme care should be maintained at all times to protect instruments from dust and from chipping and breaking of the optical parts by hard usage.

In spite of the many possible sources of instrumental errors, most carefully designed instruments are capable of greater precision of measurement than the reproducibility of the colors to be measured. That is, such errors as deviations from Beer's law; inaccuracies in weighing, volume measurements, and the like; instability of the colored material toward heat, light, air, or with time; and incomplete reaction or competing side reactions, may cause greater deviations than the instrumental errors. Careful study of the conditions under which a colored compound may be prepared reproducibly is indicated; and, once the conditions have been established, they must be adhered to rigorously. For very careful work it is usually necessary to construct calibration curves using several known solutions rather than to rely on Beer's law calculations.

With carefully designed instruments and properly chosen methods it is possible to attain a precision of from 1% to several tenths per cent with photoelectric filter photometers.

There are hundreds of examples of the use of the photoelectric colorimeter. The reader is referred to the books listed in the references for specific examples.

FLUORESCENCE METERS

When some compounds are irradiated by light of certain frequency or range of frequencies, they emit light of lower frequency (longer wavelength). The extra energy is retained by the compound, usually in the form of heat. The emitted light is spoken of as fluorescent light if it is emitted with no time delay; otherwise it is known as phosphorescent light. For very low concentrations of substances, the intensity of the fluorescent light is proportional to the concentration of the substance, if the level of illumination remains constant. At higher concentrations several factors tend to destroy the linear relationship between concentration and intensity. Some of these factors are:

1. The exciting light is absorbed by the molecules, and thus the molecules far removed from the light source are not irradiated as intensely as those near the source.
2. The fluorescent light may be absorbed to some extent by the solvent and by the other molecules it encounters before it leaves the cell.
3. Solvation, intermolecular attractions, etc., may cause changes in the characteristics of the fluorescing molecules.

Many fluorescing substances are very sensitive to the presence of other inhibiting ions, which diminish or extinguish the fluorescence. Uranyl salt solutions, for example, are very sensitive toward iodide ion and this effect can, in fact, be used to determine the concentration of the iodide or inhibiting ion.

Measurement of the intensity of fluorescence is a convenient and rapid method for the determination of a number of specific substances. Riboflavin and thiamin are commonly determined in this manner. Riboflavin fluoresces in aqueous solution. Thiamin must first be oxidized by alkaline ferricyanide solution to thiachrome which fluoresces in butanol solution. Many inorganic ion complexes with organic molecules fluoresce, especially the salts of aluminum, gallium, zinc, and magnesium with 8-hydroxyquinoline. These compounds can be determined either as a turbidity which fluoresces[3] or in solution in some organic solvent.[4]

3. Merritt, L. L., Ind. Eng. Chem., Anal. Ed., 16, 758 (1944).

4. Sandell, E. B., ibid., 13, 844 (1941). See also Sandell, E. B., "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, 1944, pp. 95, 239.

In order to adapt a photoelectric colorimeter to serve as a fluorescence meter it is only necessary to make a few minor changes. The receiving photocell is moved to a position at right angles to the entering light in order that it will not be affected by the primary light. Usually two photocells are connected in parallel or a reflecting mirror is used to increase the sensitivity. In order to further protect the fluorescent pick-up cells from the primary light which may be reflected or scattered toward them, secondary filters are placed in front of the cells. These secondary filters must be so selected that they will absorb the primary light but transmit the fluorescent light. The wavelength region of the primary light is restricted by a primary filter. The optical arrangement of the Lumetron Fluorescence Meter is shown in Fig. II-20. This fluorescence meter can be quickly converted to a colorimeter. An attachment for converting a Beckman Spectrophotometer to a fluorescence meter is available from the manufacturer.

Since many animal and plant materials fluoresce it is often necessary to isolate the desired material carefully before making the fluorescent determination. In many procedures, the total fluorescence of a mixture is first determined; secondly, the desired substance is destroyed or converted to a nonfluorescing substance, and the residual fluorescence is measured. The difference between the two fluorescence readings is taken as the amount due to the substance desired. The exciting light sometimes slowly destroys the fluorescing material. In such cases, it is desirable to use weaker light sources and more sensitive measuring devices or it is necessary to measure the fluorescence at several definite periods of time after the sample is put into the meter and to extrapolate the plot of fluorescence versus time back to zero time.

A fluorescence meter must be calibrated in terms of the substance to be determined. Several standard solutions must, therefore, be prepared. In order to quickly readjust the meter to some definite setting, it is convenient to use a piece of uranium glass or some stable solution such as quinine or dichlorofluorescein which can be placed in the meter while the meter is reset at, say, 100% reading. A blank containing all of the reagents but no standard should be used to adjust the zero of the instrument.

LABORATORY WORK WITH PHOTOELECTRIC FILTER PHOTOMETERS

Effect of Light Variations on Balanced Photoelectric Colorimeters. In photoelectric colorimeters the photocurrent usually varies as the third or fourth power of the lamp voltage. Thus, it is preferable to employ a balanced two-cell instrument in order to compensate adequately for light source variations. However, not all measuring circuits will automatically compensate for variations in the intensity of the light source even though two cells may be employed.

Apparatus. Any colorimeter equipped with two barrier-layer cells.

Microammeter of low internal resistance, Weston No. 322; or a low resistance galvanometer.

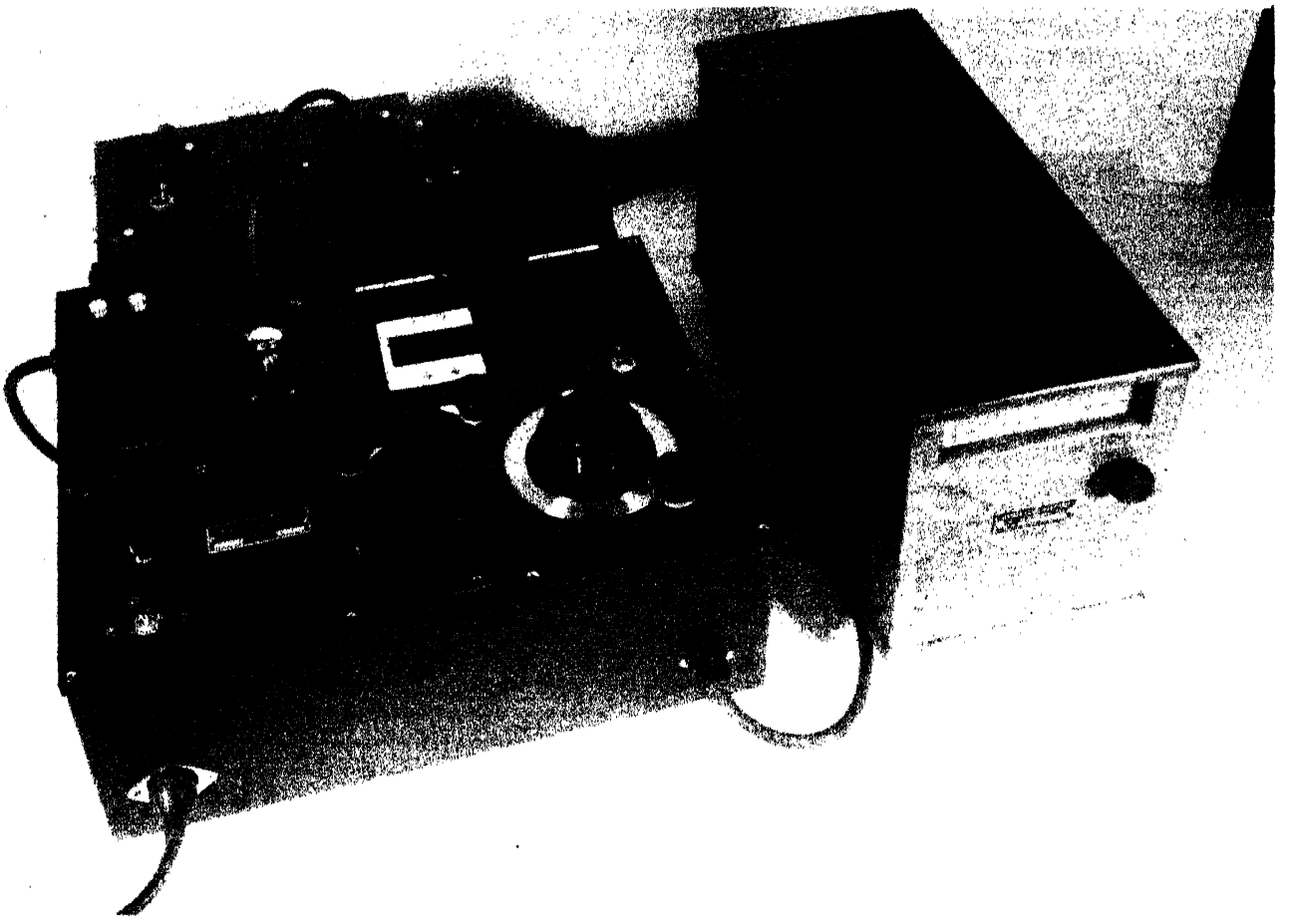
Variac. Two resistance boxes, potentiometer slide wires, or radio potentiometers, 0 to 100 ohms resistance.

Barrier-Layer Cells in Opposition.[5] Disconnect the two photocells from the colorimeter circuit. Connect one of the cells, by a suitable length of wire leading from the inside of the colorimeter, to the current measuring device and vary the voltage of the instrument's light source by means of the variac until the meter reads nearly full scale. Now connect the other barrier-layer cell to the meter so that the current from this cell flows in opposition to the current from the first cell. Reverse the polarity of the meter, if necessary, to obtain a positive meter reading; but do not change the polarity of the cells with respect to each other.

Vary the voltage of the light source with the variac and read any changes in meter deflection. Plot these readings as a function of lamp voltage. Place a neutral grey filter in the path of one of the light beams and repeat the measurement. Place different pairs of colored filters in front of each cell in addition to the neutral grey filter before one of the cells and repeat the measurement. Note that the compensation attained depends on the match obtained with the two-cell combination and that the compensation becomes progressively poorer as the differences in the illumination of the two cells becomes greater.

Barrier-Layer Cells in a Bridge or Potentiometer Circuit. Connect the two cells either as shown in Fig. II-10 or Fig. II-11. Set R_1 and R_2 to 100 ohms, and adjust R_1 or R_2 until the meter reads zero. Study the effect of lamp voltage variation by varying the voltage of the light source with the variac and read any changes in

5. Adapted from Müller, R. H., Garman, R. L. and Droz, M. E., "Experimental Electronics," Prentice-Hall, Inc., Ch. 3, pp. 72-73. Additional experiments involving photocells are included by these authors in their book.



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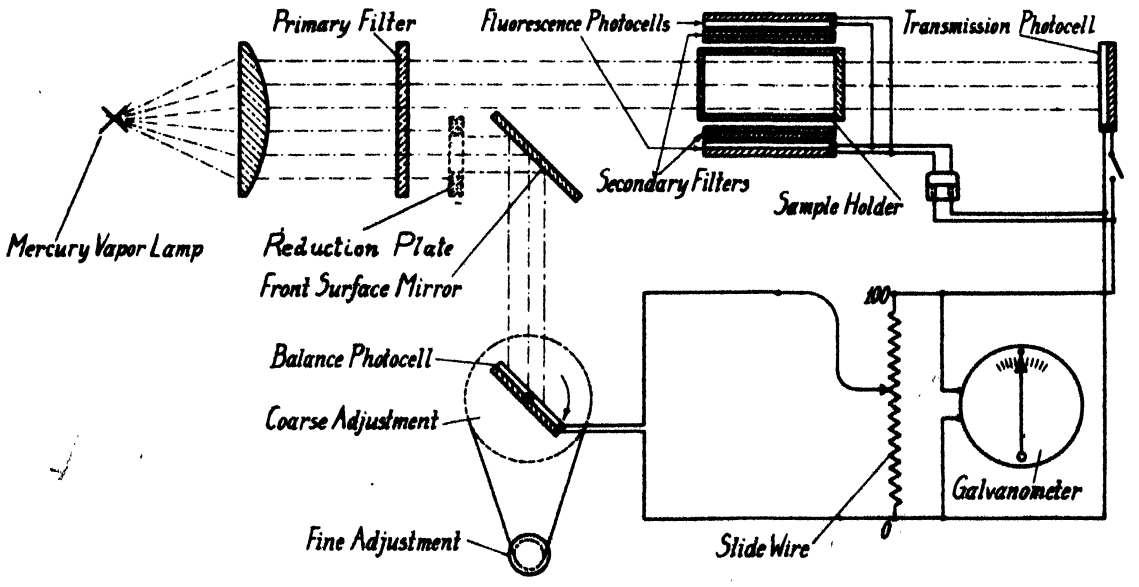


B

Fig. II-20. Lumetron Fluorescence Meter (Courtesy of Photovolt Corp.)

meter deflection. Plot these readings as a function of lamp voltage. Insert a neutral grey filter before one of the cells, and change the value of R_1 or R_2 until the meter again reads zero. Vary the voltage of the light source with the variac and read any changes in meter deflection. Repeat the measurements with different pairs of colored filters before each cell. Note that the cells now become compensating even when the illumination reaching the two cells is unequal.

General Directions for Operation of the Klett-Summerson Photoelectric Colorimeter.[6]

1. Before turning the colorimeter lamp on be sure that a filter is in place in the space provided for it between the lamp housing and the instrument proper. Adjust the pointer to coincide with the line on the pointer scale by means of the small knob on the top of the instrument. This knob must be used only when the colorimeter lamp is off.
2. Attach the electric cord to a 110 volt, A.C. outlet.
3. Flip the short circuit switch on the side of the instrument to the ON position.
4. Place a clean colorimeter tube containing distilled water in the instrument.
5. Turn the scale to zero by means of the large knob on the front of the instrument.
6. Switch on the colorimeter lamp by means of the lamp switch located on the front of the lamp housing.
7. Turn the zero adjustment knob, which is located on the top of the colorimeter to the left of the test tube, until the pointer is brought back to zero on the scale. Allow a few minutes for the lamp to warm up and again check the zero adjustment. If the pointer does not move as the zero adjustment knob is turned, the short circuit switch is probably in the wrong position.
8. Remove the distilled water tube, and place the colorimeter tube containing the standard solution in the instrument. Turn the scale knob until the pointer returns to zero. The reading on the scale at this point is the reading of the standard solution.
9. Repeat step 8, above, using the unknown solution.
10. The concentration of the unknown is directly proportional to the scale reading since the scale is logarithmic. The concentration is determined by reference to a previously determined standard curve. A somewhat less precise method is to use only one standard solution. The concentration of the unknown is then determined by multiplying the unknown reading by a factor determined from the standard reading. Thus

$$C_u = \text{reading of unknown} \times \frac{C_s}{\text{reading of standard}}$$

6. Adapted, by permission, from the instruction book furnished by Klett Manufacturing Co.

Preparation of Solutions for Laboratory Work with Photoelectric Filter Photometers

Colorimetric Determination of Iron with o-Phenanthroline. There is no lack of colorimetric reagents for iron; some react with ferric iron, others with ferrous. Better results can frequently be obtained from the latter group, since ferrous iron does not form as many stable complexes. Such is the sensitive reaction between o-phenanthroline and ferrous iron involving the formation of an orange-red complex. The color intensity is independent of the acidity in the pH range 2 to 9 and is stable for long periods. Beer's law is closely followed for concentrations from 0.1 to 5 p.p.m., using 1.00 cm. absorption cells.

Copper, nickel, and cobalt interfere seriously, other ions interfere to a lesser extent although possibilities for altering pH or using complexing agents to avoid interferences are known.[8]

Solutions Required. Hydroxylamine hydrochloride, 10% aqueous solution; or Hydroquinone, 1% solution in 0.05 M sodium acetate buffer at pH 4.5; discard either if a coloration appears.

1,10- phenanthroline, 0.5% aqueous solution.

Sodium acetate, 2 M and 0.2 M solutions.

Procedure. Measure by volume a quantity of sample containing 0.5 mg. or less of iron into a 100 ml. volumetric flask. Determine, by the use of a similar aliquot portion containing a few drops of bromophenol blue, the volume of sodium acetate required to bring the pH to 3.5 ± 1.0. Add the same volume of acetate to the working aliquot and then 4 ml. each of hydroquinone and o-phenanthroline solutions. Dilute to volume, mix well, and allow to stand for 1 hour. Measure by suitable means, using a filter with a maximum transmittance at 480 to 520 mμ.

If hydroxylamine hydrochloride is used as a reducing agent, add 5 ml. of 10% solution, heating if necessary to reduce the iron, and then 4 ml. of o-phenanthroline to a solution with pH 3 to 6 adjusted with sodium acetate. Dilute to volume, mix well, and measure after letting it stand 5 to 10 minutes.

Colorimetric Determination of Magnesium with Titan Yellow. This procedure is based upon the formation of a red lake when magnesium hydroxide is precipitated with sodium hydroxide in the

8. Sandell, E. B., "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, 1944, pp. 271-273.

presence of titan yellow, the sodium salt of dihydrothio-p-toluidine sulfonic acid. Fairly stable colloidal suspensions of the lake are obtained with magnesium concentrations from 0.2 to 3 p.p.m. Color fading is prevented by the presence of hydroxylamine hydrochloride. Beer's law holds only over a narrow range in which there is a sufficiently large excess of reagent. The method requires the absence of most other metals and any appreciable amounts of ammonium salts.

Solutions Required.
Gelatin, 1% aqueous solution.
Hydroxylamine hydrochloride, 5% aqueous solution.
Sodium hydroxide, 1 N.
Titan yellow A, 0.05% aqueous solution.

Procedure.[9] Pipet into a 50 ml. volumetric flask a quantity of sample containing 0.3 mg. or less of magnesium. Add 1 ml. of hydroxylamine hydrochloride, 5 ml. of 1% gelatin solution, and 1.00 ml. of Titan yellow solution. Dilute to 30 or 40 ml., and add 5 ml. of sodium hydroxide while swirling the solution. Dilute to volume, mix well, and measure by suitable means. A 550 mμ filter is recommended for filter photometers. The reagent alone gives a yellow-brown color in sodium hydroxide solution.

Colorimetric Determination of Nickel with Dimethylglyoxime. The procedure for the colorimetric determination of nickel differs from the gravimetric methods chiefly in the oxidation to a higher valence state by bromine water before addition of dimethylglyoxime to an ammoniacal solution. In this quadrivalent state nickel forms a red, soluble complex. Beer's law applies for concentrations from 0.1 to 5 p.p.m. of nickel, using 1.00 cm. absorption cells. An aqueous solution is unstable, but sufficient ethanol makes the color stable for 30 minutes.

Of the ions soluble under the conditions used, only cobaltous, auric, and dichromate interfere seriously. Metals which precipitate in ammoniacal solution can be removed by double precipitation, by extraction of nickel (II) dimethylglyoxime in chloroform, by use of complexing agents, or by other suitable reactions.[10]

Solutions Required.
Ammonium hydroxide, specific gravity, 0.88.
Bromine water, saturated aqueous solution.
Dimethylglyoxime, 0.1% solution in ethanol.
Ethanol, 95% undenatured.

Procedure. Weigh or measure by volume a quantity of sample containing 0.5 mg. or less of nickel into a 100 ml. volumetric flask. Make the system just acidic by means of hydrochloric acid and/or ammonium hydroxide. Add bromine water until a faint yellow color persists, then 2 ml. in excess. Then add 10 ml. of concentrated ammonium hydroxide, 35 ± 5 ml. of 95% ethanol, and 20 ml. of 0.1% dimethylglyoxime reagent. Dilute to volume, mix well, and measure by suitable means. A 440-450 mμ filter is recommended for filter photometers.

Colorimetric Determination of Phosphorus by Molybdenum Blue Procedure. One of the most frequently used methods for the colorimetric determination of phosphates is the so-called molybdenum blue procedure, which depends upon the formation of heteropoly molybdiphosphoric acid, with subsequent reduction to a blue system of uncertain composition. As the blue color formed is unstable, certain precautions must be observed; the optimum pH is 3.0 to 4.7, and full color development is complete after 30 minutes. Beer's law applies for concentrations from 1 to 15 p.p.m. of phosphorus, using 1.00 cm. absorption cells.

All strong oxidizing agents and reducing agents must be absent; also other materials which would form heteropoly acids, such as silicates, arsenates, and tungstates. Several other metallic ions also interfere.[11]

Solutions Required. Ammonium molybdate: Dissolve 5.0 g. of reagent grade ammonium molybdate in 80 ml. of water and add to this solution one containing 2.8 ml. of concentrated sulfuric acid in 20 ml. of water. Do not use if a white residue separates.

Hydroquinone: 0.5%, containing 1 drop concentrated sulfuric acid per 100 ml.

Sodium Sulfite: 11% aqueous solution.

Procedure. Measure by volume a quantity of sample containing 1.5 mg. or less of phosphorus into a 100 ml. volumetric flask. Add enough water to make the total volume at least 50 ml. Add in order, and with constant mixing, 10 ml.

9. Sandell, E. B., "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, 1944, p. 307.

10. Mitchell, A. M. and Mellon, M. G., Ind. Eng. Chem., Anal. Ed., 17, 380 (1945); Sandell, E. B. and Perlich, R. W., ibid. 11, 309 (1939); Haim, G. and Tarrant, B., ibid., 18, 51 (1946); Sandell, E. B. "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, 1944, p. 341.

11. Kitson, R. E. with Mellon, M. G., Ind. Eng. Chem., Anal. Ed., 16, 466 (1944).

of 5% ammonium molybdate solution in 1N sulfuric acid, 10 ml. of 0.5% hydroquinone solution, and 10 ml. of 11% sodium sulfite solution. Dilute to the mark and mix well. Allow the solution to stand 30 minutes and then measure the color by suitable means. A filter with a transmittance maximum between 600 and 700 mμ is recommended for filter photometers.

If the final pH does not lie between 3.0 and 4.7, make suitable adjustment in the amount of the molybdate or sulfite reagent.

CHOICE OF CORRECT FILTER IN PHOTOMETRY

In photometric applications a filter is used to isolate as narrow a band of light as is feasible, and this band must be centered as closely to the point of minimum transmittancy of the sample as possible. If a spectrophotometer is available, the wavelength of minimum transmittancy of the colored material is found from the transmittancy-wavelength curve of the material. However, in some instances a spectrophotometer may not be available, and the operator must then determine by some other means the correct filter to employ.

Apparatus and Reagents. A photoelectric filter photometer and a set of filters covering the range from 390 mμ to 760 mμ.

The necessary solutions required to develop the colored material according to the directions included for the systems: Iron, magnesium, nickel, or phosphorus, as given on pages 23 to 24; or any other system assigned by the instructor.

Procedure. 1. Prepare a series of four or five solutions of the particular colorimetric system assigned, each solution containing a different known concentration of the coloring component.

2. Hazard a rough guess as to the complementary color of the solution, and then select a set of filters whose maximum transmittancies fall in the region of the complementary color.

3. Insert the selected filters into the photometer, one at a time, and measure the optical density of each of the prepared colorimetric solutions.

4. Plot the optical density against the corresponding concentration of each solution. The filter exhibiting the maximum change in optical density per unit change in concentration will generally be the most satisfactory. If the slopes are not straight lines, the colorimetric system probably does not obey Beer's law.

LABORATORY WORK WITH PHOTOELECTRIC FLUORESCENCE METERS

General Directions for Operation of the Lumetron Model 402EF Fluorescence Meter.[12] Refer to Fig. II-21 for a top view of the operating controls of the instrument.

1. Insert the male 4-prong plug of the galvanometer cable into the socket on the right-hand side of the front wall of instrument housing.

2. Be certain that the blue leads of the galvanometer cable are connected to the binding posts marked "6 volts." Connect black and red leads to the respective posts marked "Galv." If the galvanometer is not already connected as described, call the attention of the instructor to it. A wrong connection will burn out the expensive galvanometer.

3. Insert female plug of power cord into the male socket on the left side of front wall of instrument housing.

4. Be sure that the mercury vapor lamp and not the tungsten lamp is installed in the light housing. Insert the plug from the mercury light into the transformer and turn the switch on the transformer to 115 volts.

5. Insert male plug of power cord into 110 volt, 50-60 cycle, A.C. line. Turn on the fan motor.

6. Place the square, black block with felt on one side in front of the photocell at the right of the solution chamber. Place the felt side of the block away from the photocell.

7. Insert the transformer plug into a 110 volt, 50-60 cycle, A.C. line. This lights the mercury lamp. Allow several minutes for the light to warm up, and do not turn the light off until ready to stop or to leave the instrument for some time.

8. Throw switch FT, below the solution chamber, to the left.

9. Plug the fluorescence pickup unit into the socket, R, in the solution chamber.

10. Insert the primary filter into the filter holder so that the label is away from the operator. Slide the secondary filters in front of the two photocells of the fluorescence pickup unit.

11. Set the galvanometer to zero or to some value near zero by means of the knob on the front of the galvanometer housing.

12. Place the sample holder with standard solution into the pickup unit with the thin window toward the light source. Slide the sample holder to the left as far as it will go. The solution level should be above the lower edge of the top plates of the pickup unit (25

12. Adapted, by permission, from the instruction book furnished by Photovolt Corporation.

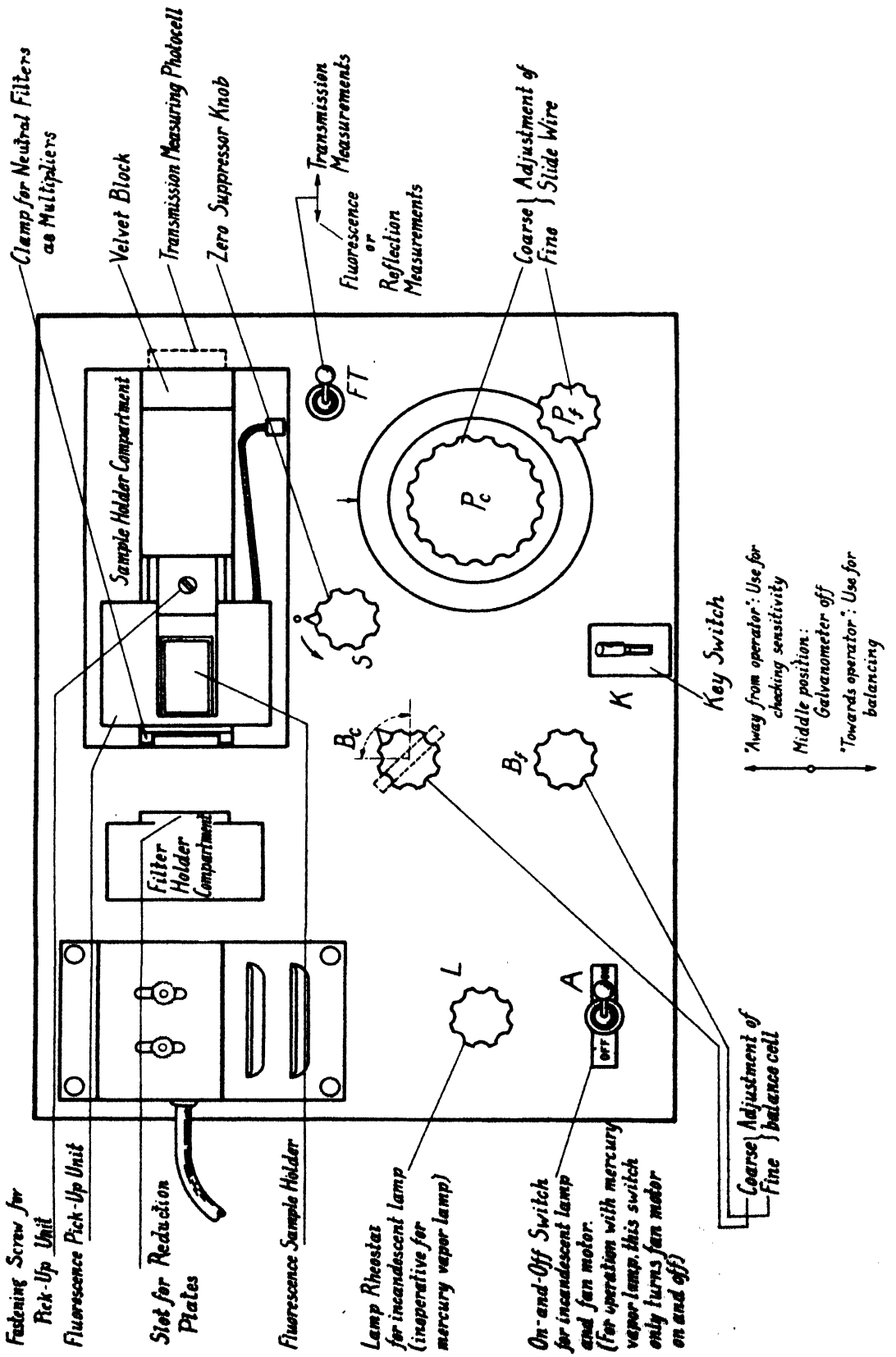


Fig. II-21. Top view of operating controls of Lumetron Model 402EF Fluorescence Meter (Courtesy of Photovolt Corp.)

ml. for large size holder is correct). Close the cover of the compartment.

13. Push the key switch, K, "away from operator." The galvanometer should deflect to the right. If it does not, reverse the black and red leads only of the galvanometer.

14. Set slide wire to 100. Pull key, K, "toward operator" and adjust the balance cell controls, Bc and Bf, until the galvanometer reads near zero. If the control knob is near its clockwise end position, insert a suitable reduction plate into slot on right-hand side of filter compartment and push the plate all the way down. The smallest aperture should be selected for which it is still possible to obtain a balance.

15. For final balancing, proceed as follows: Release key switch and note the exact position of the light spot on the galvanometer scale. Pull key switch "toward operator" and adjust the balance cell control knob (fine adjustment) until the light spot is back in the noted position (disregard slight temporary movements and observe only the position of the spot when it is at rest.)

16. Insert a blank solution in place of the standard.

17. Set slide wire on zero.

18. Note position of light spot when key is released. Pull key "toward operator" and adjust the zero suppressor knob until the light spot is back in the original position.

19. Insert the unknown solution in place of the blank.

20. Pull key "toward operator" and adjust the slide wire until the galvanometer reads near zero. Release the key and note the exact position of the light spot. Pull key "toward operator" and readjust the slide wire carefully. The slide wire now reads per cent fluorescence in terms of the standard.

Notes: Be careful not to turn the slide wire dial beyond 0 or 100. Too concentrated solutions do not give linear response to fluorescence to concentration. If the unknown is concentrated, it should be diluted rather than a more concentrated standard solution prepared.

General Instructions for the Operation of the Klett-Fluorimeter (adapted from the instructions furnished by the manufacturers).

Instrument Design. Observe Fig. II-22. The housing at the right contains the reference photocell, the green (Corning #4080) light filter, and an adjustable diaphragm. The housing at the left contains the measuring photocell, the photocell or secondary fluorescent light filter, the photocell mask, the solution cuvette, the exciting lamp or primary light filter, a shutter, and condenser lenses. The mirror facing the solution cuvette increases the measuring photocell response about 40%.

The lamphouse at the rear of the instrument is removed by pulling straight up. Underneath is the socket holding a type H-4 high-pressure mercury lamp. The lamp becomes very hot after it has been operated for a few minutes, and it is advisable to cool it with an air jet. NEVER OPERATE the lamp with the housing removed because the intense light is harmful to the eyes, and the lamp sometimes fails by exploding.

The potentiometer knob and scale and the two-position galvanometer switch are located on the instrument panel between the two side housings. An external lamp and scale galvanometer is used for null point balancing.

Procedure. 1. Set the switch in the top of the special transformer to the value nearest the line voltage. Plug the transformer cord into the 110-115 volt, 60 cycle, A.C. line. The fluorimeter lamp is connected to a polarized cap; plug the cap into the polarized receptacle in the front of the transformer housing. Turn on the transformer switch and the lamp will light in a few seconds. The lamp should burn for at least 5 minutes before any readings on the instrument are attempted.

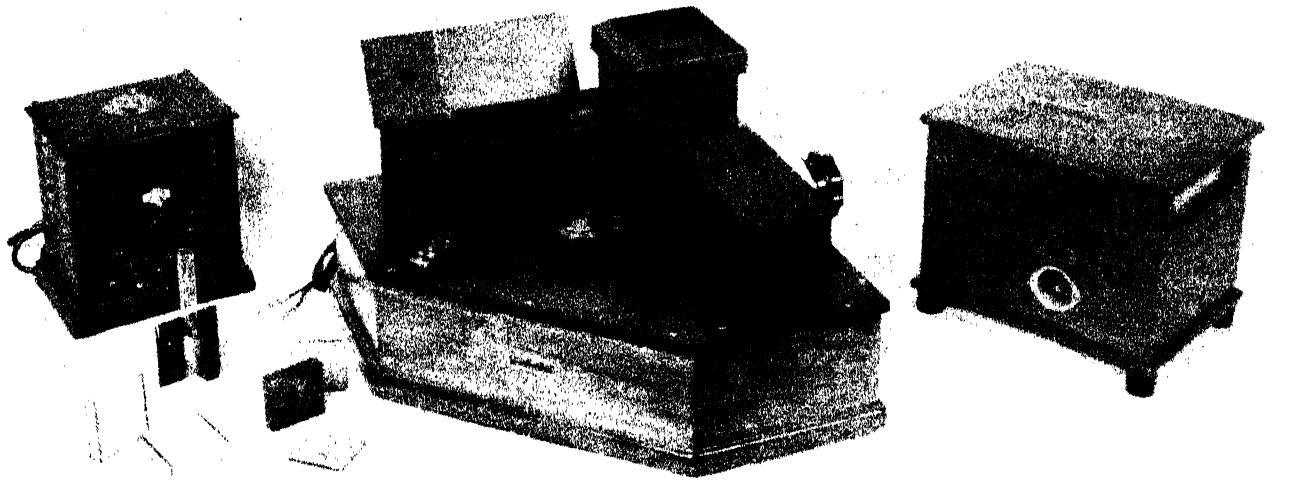
2. Connect the galvanometer leads to the two binding posts on the galvanometer. (Never move a taut suspension galvanometer unless the galvanometer terminals are short-circuited by a piece of wire.) Plug the galvanometer light cord into the other receptacle of the duplex receptacle in the transformer housing. If the spot of the light beam is not near the center of the scale, move it to some convenient point by means of the long handle on top of the galvanometer, or by sliding the glass scale.

3. Lift the two lids off the instrument housing at the left. Place the primary lamp filter (Corning #5970 or suitable substitute) in the place provided and put an appropriate secondary photocell filter between the photocell and cuvette mask.

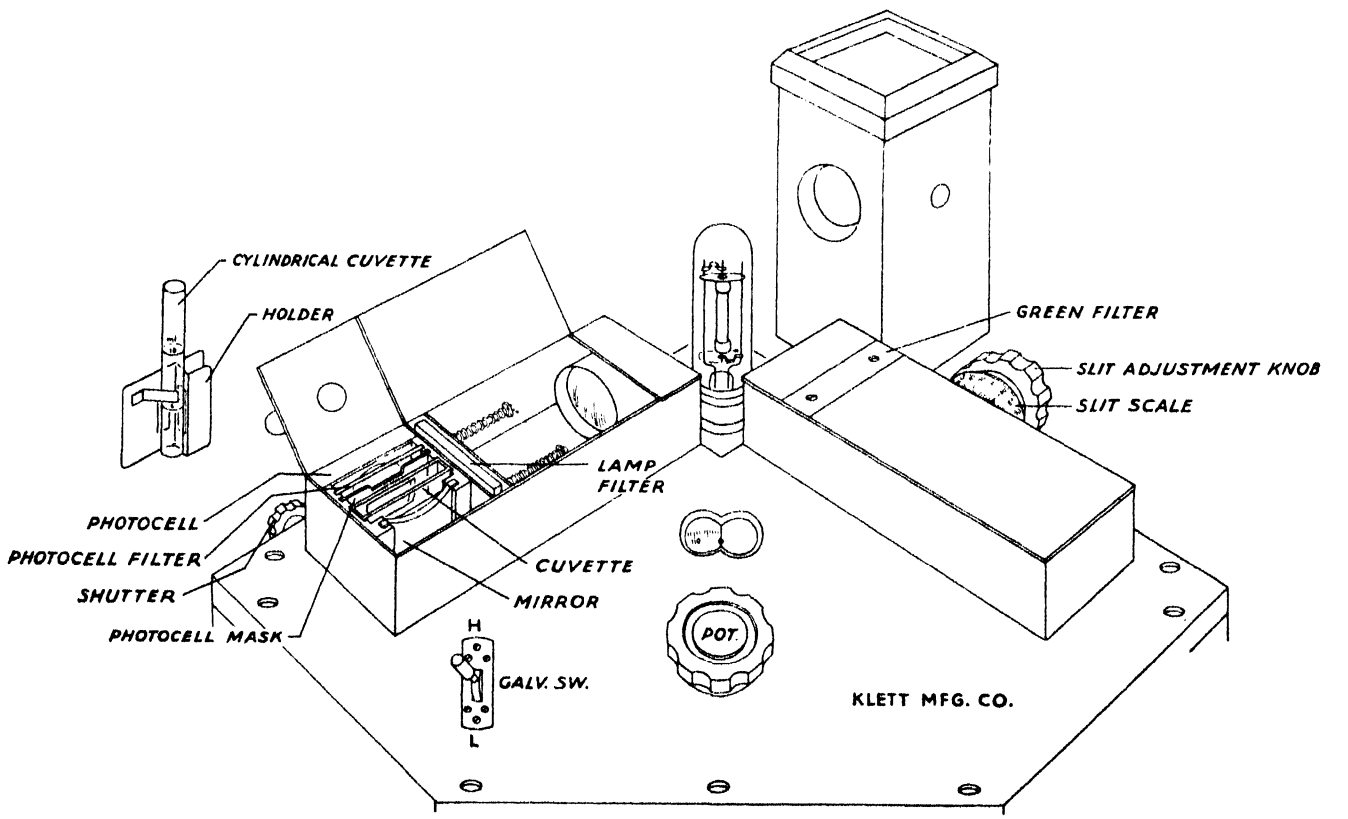
4. Fill the cuvette with the standard fluorescent solution and put the cuvette in place.

5. Pull out the small knob on the left side of the fluorimeter case, thus opening the shutter. This shutter should be kept closed except during the time that measurements are being made. Close the two lids on the left housing.

6. Set the potentiometer to some convenient value, usually between 100 and 200. Open the shutter, move the galvanometer switch to the "L" (low sensitivity) position, and adjust the variable slit on the right housing until the galvanometer returns to the middle portion of the scale. Move the galvanometer switch to the "H" (high sens-



A



B

Fig. II-22. Klett Fluorimeter (Courtesy of Klett Manufacturing Co.)

itivity) position and readjust the variable slit until the galvanometer spot returns to the original rest position. Close the shutter.

The instrument has now been standardized against the known fluorescent standard, and the variable slit does not have to be changed until the range of the instrument is changed, or a new system or standard is used. When the scale of the adjustable diaphragm indicates 100, the diaphragm is fully open; a reading of zero indicates a closed diaphragm.

7. Open the lid on the left housing and re-

place the cuvette with one containing the unknown, the fluorescence of which is to be measured. Close the lid and open the shutter. Move the galvanometer switch to "L" and turn the potentiometer knob until the galvanometer light spot returns to the rest position. Repeat the potentiometer adjustment with the galvanometer switch in the "H" position until the light spot returns to the rest position.

8. Return the galvanometer switch to the vertical position and close the shutter. The ratio of the potentiometer scale reading to that of the standard gives the ratio of the fluorescence of the unknown to that of the standard.

Notes: For most work choose a value of standard and potentiometer reading such that a deflection of 1 mm. on the galvanometer scale is obtained when the potentiometer is moved from the balance point by 2 or 3 divisions. In general, the larger the potentiometer setting for standardization and the lower the concentration of the standard, the less is the sensitivity.

When the full scale represents a low concentration of fluorescence, the calibration curve relating concentration and potentiometer reading is a straight line. When the full scale of the potentiometer represents a high concentration, the calibration curve is curved toward the concentration axis for the higher concentrations.

The path of the ultraviolet light through the cuvette should be down the center of the cuvette when the cuvette is viewed from above. Move the lamp if it is necessary to center the light beam, but only after the lamp has been turned off.

PREPARATION OF SOLUTIONS FOR LABORATORY WORK WITH FLUORESCENCE METERS

Determination of Riboflavin. This is a greatly simplified procedure since the unknowns consist of dilute acetic acid solutions of pure riboflavin. No separations are necessary, and no interferences from other fluorescing substances have to be considered.[13]

Solutions Required: Standard riboflavin solution; Dissolve 10 mg. of riboflavin in 1000 ml. of 1% acetic acid solution. This solution should be kept cool and in the dark. This solution contains 10 micrograms of riboflavin per milliliter.

13. For a determination of riboflavin in biological materials, see Hodson, A. Z. and Norres, L. C., J. Biol. Chem., 131, 621 (1939).

Procedure. Prepare a standard riboflavin solution containing not more than 1 microgram of riboflavin per milliliter by diluting a small amount of the standard solution with distilled water. For a blank, use distilled water. Use the unknown itself, or a dilution of it, if it is too concentrated. Report the number of micrograms of riboflavin per milliliter of unknown solution.

$$C_u = C_s \times \% \text{ fluorescence}$$

Determination of Zinc

Solutions Required. Standard zinc solution: Dissolve a weighed amount (about 4 g.) of C.P. zinc in 35 ml. concentrated hydrochloric acid and dilute to 1 liter. Prepare less concentrated standards by volume dilutions.

8-Hydroxyquinoline, 5%. Dissolve 5 g. of C.P. 8-hydroxyquinoline in 12 g. of glacial acetic acid and dilute to 100 ml. with distilled water.

Gum Arabic, 2%. Grind 2 g. of gum arabic in a mortar until fine and dissolve in enough water to make 100 ml. Filter if not clear.

Ammonium Acetate, 2N. Dissolve 154 g. of crystallized ammonium acetate in water to make 1 liter.

Standard Dichlorofluorescein. A 0.1% alcoholic solution of dichlorofluorescein is added drop by drop to 1 liter of water until the resulting solution has a fluorescence approximately the same as that produced by a turbidity from 0.30 mg. of zinc in the manner described below. About 0.35 ml. of dichlorofluorescein solution is required.

A narrow band filter of 420 mμ maximum transmittance is used in the primary beam, and amber secondary filters are used in front of the measuring cells.

Construct a calibration curve for the instrument by using amounts of the standard zinc solution containing between 0.05 mg. of zinc and 0.50 mg. of zinc. Four points should be sufficient.

Place the standard zinc solution or 10 ml. of the unknown solution in a 50 ml. volumetric flask. Add 5 ml. of 2 N ammonium acetate and 2 ml. of a 2% solution of gum arabic. Dilute with distilled water to approximately 45 ml. and mix by swirling the flask. Using a serological pipet, add exactly 0.20 ml. of 5% 8-hydroxyquinoline solution. Dilute to the mark with distilled water, shake gently, and pour into the cell of the instrument for measurement.

Adjust the instrument according to the general instructions so that the dichlorofluorescein solution reads 50.0 and a blank containing no zinc but all reagents reads 0.0. A turbidity of zinc prepared as above and containing 0.30 mg. of zinc

may also be used for adjusting the instrument to 50.0. (It is sometimes more convenient to standardize the instrument at 50 rather than 100.)

Read the amount of zinc in the unknown from the calibration curve (plot reading vs. mg. of zinc present). Report as mg. of zinc per ml. of unknown solution.

Determination of Aluminum. A rapid fluorometric method has been developed by Weissler and White[14] for the quantitative determination of from 0.001% to somewhat over 1% of aluminum in steels, bronzes, and minerals. The preferred reagent is the dyestuff Pontachrome Blue Black R, which is used at a pH of 4.8 in a buffered solution. Beryllium gives no fluorescence and does not interfere in any way, nor do most other ions. Copper, chromium, iron, nickel, and cobalt mask the fluorescence, and fluoride ion must be removed if present.

Apparatus and Reagents. A narrow band 365 mμ filter is used to isolate the ultraviolet exciting radiation, and sheets of red plastic or glass to isolate the red fluorescent light emitted.

Standard solution of aluminum, 1.00 ml. = 0.0100 mg. Dissolve 0.1760 g. of potassium aluminum sulfate crystals in water and dilute to 1 liter.

Weaker standard solution of aluminum, 1.00 ml. = 0.00100 mg. Pipet out 100 ml. of the above solution and dilute to 1 liter.

Ammonium acetate solution, 10%. Dissolve 50 g. of the salt in water and dilute to 500 ml.

Pontachrome Blue Black R (color index 202), 0.1% solution. Dissolve 0.50 g. in 500 ml. of 95% ethanol and allow to stand a few days before using. The dye is obtainable from Du Pont.

Dilute sulfuric acid, 1 to 9. Pipet 100 ml. of concentrated acid into several hundred milliliters of water in a 1 liter volumetric flask, cool, and dilute to the mark.

Procedure. This is a greatly simplified procedure since the unknowns consist of very dilute aqueous solutions of pure aluminum salt. No separations are necessary, and no interferences from other fluorescing substances have to be considered. For a determination of aluminum in steels, bronzes, and minerals, consult the original paper.

Pipet a suitable aliquot of the unknown sample into a 50 ml. volumetric flask containing 5.0 ml. of 10% ammonium acetate, 0.50 ml. of 1 to 9 sulfuric acid, and 1.50 ml. of 0.1% Pontachrome Blue Black R, and dilute to the mark. Let stand for 1 hour, and then measure the fluorescence and compare with that of standards prepared similarly and simultaneously. Convenient concentrations of aluminum in the standards are 0.00500, 0.0100, 0.0150, 0.0200, and 0.0250 mg. per 50 ml. volume. Calibrate the fluorescence meter with the standard containing 0.0250 mg. with the transmission scale set at 100.

Report the number of micrograms of aluminum per milliter of unknown solution.

14. Weissler, A. and White, C. E., Ind. Eng. Chem., Anal. Ed., 18, 530 (1946).

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CHAPTER III

TURBIDIMETERS AND NEPHELOMETERS

The word "turbidity" as applied by the chemist is a rather difficult word to define. It refers to the characteristic optical properties of dispersions and is usually defined as a concentration, assuming that all other variables are constant. Thus the intensity of light reflected by a suspension is a function of concentration when other conditions are constant. It is a great advantage in many cases to be able to measure a precipitate without separating it from the solution. This is especially true when it is difficult to filter, wash, and dry the material, or when speed is especially desirable.

Methods of measuring turbidity fall into three groups,

1. Those which measure the ratio of intensity of the scattered light, the Tyndall light, to that of the incident light.
2. Those which measure the ratio of the intensity of the light transmitted through the solution to that of the incident light.
3. Those which measure the "extinction effect," that is, the depth at which a target disappears beneath the layer of turbid medium.

Instruments which measure the Tyndall ratio are called tyndallmeters if the intensities are measured directly and nephelometers when the same is compared with a standard of known concentration. Instruments which measure the transmitted light by either method 2 or 3 are known as turbidimeters. The Tyndall ratio is most sensitive at extreme dilutions and the extinction effect is good at high concentrations while the transmission effect occupies a middle region.

As a first approximation, the turbidity is proportional to concentration times depth. It also depends on color, which in turn depends on the particle size. For particles small compared with the wavelength of light, Rayleigh's law states that the Tyndall ratio is proportional to the cube of the particle size and inversely to the fourth power of the wavelength. Particles large compared to the wavelength of light merely reflect the light from their surfaces, and so the turbidity is proportional to their total surface.

If the turbidity is to be proportional to the concentration, then the particle size, that is, the dispersion, must be constant. One of the most difficult aspects of turbidimetry is to be able to produce reproducible dispersions. It must not be taken for granted that the same technique will always give the same turbidity with the same concentration of the dispersed phase. Careful studies must be made to find just the correct procedure to use in any application. The precipitates must be very fine so as not to settle rapidly, yet they should not be of colloidal dimensions since these are not uniform in appearance and may appear colored by transmitted light. Suspensions of large crystals have relatively low opacity, settle rapidly, and are not suitable for turbidimetric work.

The following conditions must be carefully controlled in order to produce suspensions of uniform physical character:

1. Concentration of the two ions which combine to produce the precipitate.
2. Ratio of concentrations in the solutions mixed.
3. The manner and order of mixing.
4. The time rate of mixing.
5. The amounts of other salts and substances present, especially protective colloids.
6. The temperature.

In order to produce and keep a suspension for the time necessary to make the measurements, the solution of material being determined must be dilute, not stronger than 100 mg. per liter. The precipitate should be white or nearly so; if highly colored it should be determined colorimetrically. It should be amorphous if possible, since crystalline particles may settle rapidly. A protective colloid such as gelatin, gum arabic, or starch can be added to help prevent too rapid settling.

P. V. Wells[1] sums up the requirements of a nephelometric method as:

1. It must be reproducible.
2. It must maintain a constant degree of turbidity during the time of comparison.
3. The turbidity must be completely homogeneous and the density must be kept within certain limits. If too dense, it will coagulate.
4. The ratio between the turbidities to be compared must not be greater than 1:4.

1. Wells, P. V., Chem. Reviews, 3, 331 (1927)

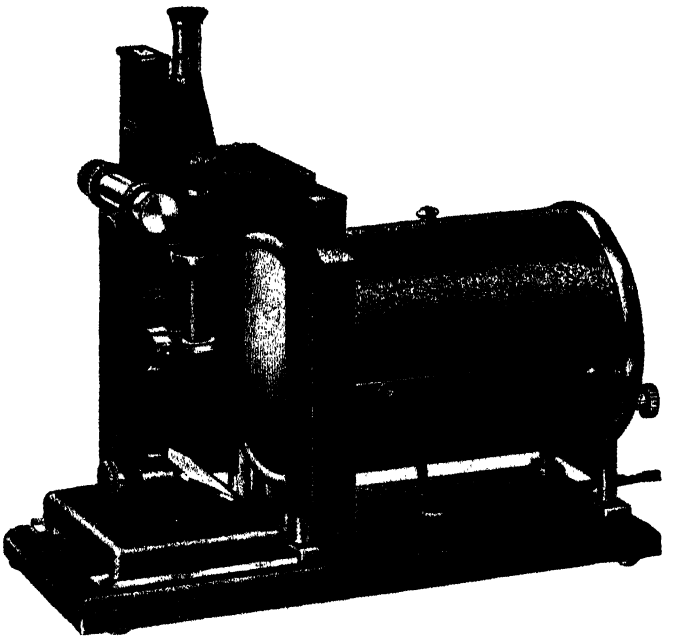
5. The turbidities to be compared must have the same dispersion, since the intensity of the Tyndall light is dependent on both the number of particles and their size. To measure one variable, the other must be constant.

Turbidimetry and nephelometry take their place along with colorimetry as extremely sensitive methods of analysis. It is a standard method of analysis and has established its usefulness on toxic smokes during the war and on the pollution of air by dust particles. Many commercial products are turbid and must be filtered. Turbidity is a convenient measure of filtration efficiency. In the biochemical analysis of blood, urine, spinal fluid, etc., the method has shown its usefulness, particularly for the proteins for which no comparable color reactions have been found. In the standardization of vaccines, and the counting of bacteria and blood corpuscles, some work has been done.

Yoe and Kleinmann[2] give methods for determination of such substances as phosphorus, ammonia, calcium, chlorine, sulfur, acetone, amylase, mustard gas, fats and oils, nucleic acids, β-oxybutyric acid, pepsin, proteins, purine bases, and trypsin.

Instruments. The first real nephelometer was designed by T. W. Richards in 1894. He used the instrument to measure small amounts of silver or halide ions in his atomic weight work. A good Duboscq colorimeter makes a good nephelometer with few changes (Fig. III-1). The sides of the cups must be clear so that the light can enter at right angles to the cups. The cups are black on the sides with clear bottoms. The light which enters at right angles to the cups must be carefully chosen and regulated so that equal illumination is obtained on both sides and no shifting takes place. The dividing line between the two fields in the eyepiece must be thin and sharp and seem to disappear when the fields are matched.

Stray light is a serious source of error in nephelometers. Dispersions are like sponges and integrate the light from every source. The instruments should preferably be in a dark room and all interior parts should be matte black. Dust and scratches on the optical parts must be avoided much more carefully than in other optical instruments. The best tests of stray light are the zero readings, both with the cups empty and with them full of optically clear distilled water.



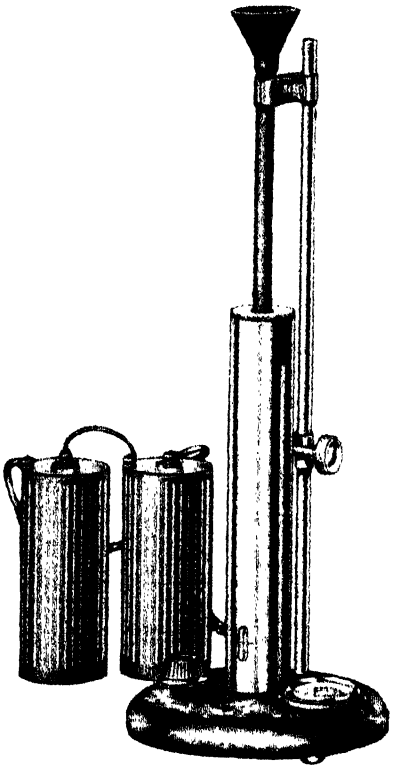
III-1. Klett Colorimeter-Nephelometer

The oldest extinction type turbidimeters are the canvas discs lowered by the oceanographer to measure the depth at which they disappear. A platinum wire which can be lowered into streams to measure clarity is now standard practice in water analysis. The Parr sulfur turbidimeter, Fig. III-2, is a good example of a visual extinction-type turbidimeter. One advantage of the disappearance method is its great range. In field work the U.S. Geological Survey standard platinum wire can be used in streams of crystal purity or in rivers of almost solid mud. The extinction criterion has been useful in measuring the covering power of paint pigments and the fineness of grain of photographic emulsions.

The visual nephelometers and turbidimeters mentioned above have now largely been replaced by photoelectric devices. Almost any photoelectric colorimeter will serve as a turbidimeter without any changes. A calibration curve must be constructed using several standard solutions since the light transmitted by a turbid solution does not always obey Beer's law precisely.

Accuracies better than 1% as claimed by many workers are probably extravagant. The instruments are capable of greater precision but the reproducibility of the turbidities is usually not

2. Yoe, J. H. and Kleinmann, H., "Photometric Chemical Analysis," Vol. II, (Nephelometry), John Wiley & Sons, Inc., New York, 1929.



III-2. Parr Sulphur Turbidimeter Visual Type

good. Much more attention and study need to be paid to the production of reproducible dispersions.

The instrument designed by Gucker, O'Konski, and Pickard[3] for measuring the concentration of dilute smokes or aerosols is noteworthy. Gucker, O'Konski, Pickard, and Pitts[4] have designed an instrument for actually counting the individual particles of an aerosol. They make use of the fact that for particles of about the same size as the wavelength of light, the light scattered in the forward direction is much greater than that scattered in the other directions.

LABORATORY WORK WITH TURBIDIMETERS

General Instructions for Parr Sulfur Turbidimeter, Visual Model[5].

1. Connect the wires from the base to three dry cells in series. Turn the rheostat knob clockwise to increase the current to the lamp. If the voltmeter backs off the scale, reverse the two battery connections. If the meter fluctuates and will not stay on a setting, clean and tighten all connections.

The voltage can be varied to suit different conditions, but is usually set at 3 volts.

2. To prepare for a test, slide the eye tube up through the clamp until it is out of the plunger tube, and swing both clamp and tube to one side. Remove the plunger tube and solution tube from the turbidimeter and see that their bottom glasses are clean and dry.

3. The solution whose turbidity is to be measured is poured into the solution tube and this and the plunger tube are replaced in the instrument. Use 200 ml. of solution.

4. Be sure the voltmeter reads 3 volts. Turn the knob to increase the depth of solution. The disappearance of the lamp filament is taken as the end point. The depth in millimeters is read on the scale on the front of the instrument. Two or three readings should be taken and averaged, but the readings should be obtained quickly before the suspension settles. Approaching the end point as a disappearance rather than appearance of the filament usually gives better results.

General Instructions for the Klett-Summerson Photoelectric Colorimeter (refer to Chapter II).

DIRECTIONS FOR PREPARATION OF SOLUTIONS FOR LABORATORY WORK WITH TURBIDIMETERS

Sulfate Determination. Since a turbidity of barium sulfate is difficult to reproduce, the prescribed conditions must be carefully observed. Work rapidly and methodically so that each turbidity is prepared under identical conditions.

Not only the concentrations of the reactants but also the velocity of the precipitation must be controlled. This is accomplished by adding (after all other components are present) the precipitant, barium chloride, in the solid form, having a definite grain size. Thus the rate of solution of the barium chloride controls the velocity of the reaction. In order to inhibit the growth of the microcrystals of barium sulfate, sodium chloride and hydrochloric acid are added before the precipitation. As the precipitation

3. Gucker, F. T., O'Konski, C., and Pickard, H., J. Am. Chem. Soc., 69, 429 (1947).

4. Gucker, F. T., O'Konski, C. T., Pickard, H. B., and Pitts, J. N., ibid., 69, 2422 (1947).

5. Adapted from the instruction book furnished by the makers.

takes place the reaction vessel is shaken in order to obtain a uniform particle size. Shake each turbidity at the same rate and the same number of times. The unknowns must be treated exactly like the knowns, and the interval between the time of precipitation and measurement must be kept constant. Unless these precautions are observed, a large experimental error will result.

A calibration curve is constructed using at least five known solutions. If a photoelectric colorimeter is employed, plot transmittancy against amount of sulfur, or, better, plot transmittancy on semilogarithmic paper against milligrams of sulfur. The reading of the Klett-Summerson instrument is already a logarithmic function. If the visual Parr sulfur turbidimeter is used, plot the depth in millimeters against milligrams of sulfur.

Solutions Required. Standard sulfate solution. Dissolve 0.5444 g. of C.P. potassium sulfate in distilled water and dilute to 1 liter. This solution contains 0.1 mg. of sulfur per ml.

Barium chloride. The crystals are sifted to pass a 20-mesh sieve and be retained on a 30-mesh sieve.

Sodium chloride solution. One liter contains 240 g. of sulfate-free sodium chloride and 20 ml. of concentrated hydrochloric acid.

Method. The cuvettes of the photoelectric colorimeters or turbidimeters may vary from 10 ml. to 100 ml. in capacity. The visual Parr sulfur turbidimeter requires 200 ml. of solution. The photoelectric turbidimeters used in the laboratory are equipped with specially selected test tubes which are more convenient to use than cemented cells. In all cases the cuvettes must be scrupulously clean and free from finger marks. Prepare turbidities within the range of 3.5 mg. to 7.0 mg. of sulfur. From a buret measure between 35 and 70 ml. of the standard sulfate solution into a glass-stoppered graduated cylinder of 200 to 250 ml. capacity. For use on a photoelectric turbidimeter, add 15 ml. of sodium chloride-hydrochloric acid solution and make up to 100 ml. For measurement on the Parr sulfur turbidimeter, add 25 ml. of the sodium chloride-hydrochloric acid solution and make up to 200 ml. Add 1 g. of barium chloride crystals (about 0.7 ml. which can be measured out quickly with the aid of a small scoop). Stopper the cylinder and shake for 1 minute by inverting the cylinder once per second. Transfer the turbidity to the absorption vessel and measure the transmittancy or the disappearance of the lamp filament, depending on the instrument. Construct the calibration curve.

Take about 25 ml. of the unknown solution and go through the above routine. This constitutes a trial run since the turbidity may be such that the reading will not fall on the calibration curve.

Avoid air bubbles in the absorption vessels. These may be removed by gently tapping the bottom of the vessel with the fingertip or by probing with a small fire-polished glass rod over the end of which is slipped a short piece of rubber tubing to prevent scratching of the optical surfaces. To clean the fragile vessels of adhering barium sulfate, use concentrated hydrochloric acid and a rubber policeman. Do not attempt to use a brush.

Phosphate Determination. In this experiment phosphorus pentoxide as phosphate is determined by measuring the transmittancy of a suspension of strychnine phosphomolybdate. This turbidity is white in color and consists of extremely fine particles in contrast to ammonium phosphomolybdate which is yellow and consists of rather large grains. The strychnine phosphomolybdate turbidity is somewhat sensitive to temperature changes which may markedly alter its useful life. This precipitate must not be agitated for it will agglomerate readily. The turbidities of strychnine phosphomolybdate are also suitable for comparison in a nephelometer.

Solutions Required. Sulfuric acid, 2N: Use only the purest acid obtainable. Dilute 54 ml. of concentrated acid to 1 liter and standardize. By making up a sufficient quantity of the acid to last as long as the calibration curve is reliable (the instrument may drift after several months of operation), one can insure that in every determination the acidity will be the same although the acid need not be exactly 2 N.

Saturated sodium sulfate solution: Saturate at 50°C. and cool to room temperature. Filter when used.

Molybdenum-strychnine reagent: This reagent is prepared in two parts. These are mixed just before using since the addition of the acid molybdate solution to the strychnine produces a sediment after 24 hours.

Solution A. Sulfuric acid-sodium molybdate solution. Place 30 g. of purest molybdic anhydride freed from ammonia by gentle ignition in a 500 ml. round-bottom flask and add 10 g. of anhydrous sodium carbonate and 200 ml. of water. Boil the mixture until a perfectly clear solution has formed. It may be necessary to add additional sodium carbonate to accomplish this. Filter

off impurities while the solution is hot. Add 200 ml. of 10 N sulfuric acid and cool. Make up to 500 ml. The pH should be 1.4.

Solution B. Strychnine solution: Dissolve 1.6 g. of strychnine sulfate (bisulfate) in 100 ml. of warm distilled water. After cooling, dilute to 500 ml.

To make the reagent, mix solutions A and B as follows: Pipet equal volumes of each into separate flasks. Add solution B quickly to A and shake thoroughly the resultant mixture. Filter off through a Whatman #42 filter the bluish white precipitate which forms. The clear, colorless solution will keep about a day. Solutions A and B may be kept indefinitely.

Standard phosphate solution: Dissolve in distilled water 0.0197 g. of potassium dihydrogen phosphate, analytical reagent, dried at 110°C., and dilute to 1 liter. This solution contains 0.01 mg. phosphorus pentoxide per ml.

Method. Take suitable amounts of the phosphate solution, for example, 2, 4, 6, 8 ml., add 9.5 ml. of the 2 N sulfuric acid, then 4 ml. of the saturated sodium sulfate solution, and dilute up to 23 ml. with distilled water. Now add 2 ml. of the strychnine molybdate reagent, swirl the solution to mix the reagents, but do not shake. Let the turbidities develop for at least 20 minutes before measuring. Plot transmittancy or scale reading against milligrams of phosphorus pentoxide per 100 ml.

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CHAPTER IV

SPECTROPHOTOMETRY AND FLAME PHOTOMETRY

The spectrophotometer is an instrument for measuring the relative amounts of radiant energy absorbed by a medium as a function of the wavelength (or frequency) of the radiant energy. It may be considered as a refined filter photoelectric photometer using continuously variable and more nearly monochromatic bands of light. Spectrophotometers must contain, therefore, the following essential parts:

1. A source of radiant energy. For a discussion of the various sources available, see Chapter II, pages 13 to 15.
2. A monochromator; that is, a device for isolating monochromatic or, more generally, narrow bands of radiant energy from the light source.
3. Cells for holding the substances under investigation.
4. A device to receive and measure the intensities of the beam or beams of radiant energy passing through the substances under investigation. For a discussion of these receiving and measuring devices, refer to Chapter II, pages 15 to 20.

Since several of the constituent parts of spectrophotometers have been previously described, it is necessary here only to describe the various types of monochromators employed and to show how the various parts are combined to form a complete instrument. Monochromators can be divided into those employing a grating as a dispersing device and those employing a prism. In every case there will be an entrance slit through which the light enters the monochromator. This entering light is then dispersed into a spectrum which is, in reality, a series of images of the entrance slit. If this spectrum is brought to focus at the exit slit, a narrow portion of the light can be allowed to pass through the exit slit and into the material being investigated. The wavelength range of the light passing through the exit slit can be varied by changing the position of the grating or prism.

The purity of the emerging light depends largely upon the sizes of the entrance and exit slits. Theoretically both should be infinitely small but then the resulting intensity would be nearly zero. In actual practice, it is necessary to use slits sufficiently large to pass enough light to be measured easily by the measuring devices. Thus the more sensitive the measuring devices, the smaller the slits can be and the purer the light. An interesting treatment of the relationship between slit width and purity is given by Hogness, Zscheile, and Sidwell.[1]

When determining the absorption curve of substances, especially those with sharp changes in the extent of absorption or with narrow absorption bands, the purity of the light used in the measurement may have a profound effect upon the curve. With a wide band of light, each measurement represents an average of the transmittancy over that band, and, therefore, narrow absorption bands may be missed completely or may appear only as inflections in the curve. For most analytical applications fairly wide bands of, say, 5 mμ may be used provided that the wavelength settings may be reproduced accurately.

Gratings, especially replica gratings, are generally cheaper than prisms and are used in the less expensive instruments for dispersing the light. Furthermore, reflection gratings can be used for all regions of the spectrum since the light does not pass through the medium. Although echelette gratings can be constructed so that 80% of the incident light energy is diffracted in a given order of spectrum on one side of the normal, there is produced, in any case, several orders of spectra. Thus, when light of 750 mμ should be passing through the exit slit, some light of 375 mμ will also be present. Such light is a special kind of stray light and may cause serious errors in the transmission measurements. Much can be done to prevent such errors by using filters before the entrance slit to remove the interfering short-wave radiation. When short wavelength light is passing through the exit slit another type of stray light error may occur. The grating is nearly normal to the entrance and exit slits in many instruments when working in the ultraviolet region, and light from the entrance slit may merely be reflected from the grating. Much of this light can be eliminated by using a filter before the entrance slit to remove the longer wavelength radiation. Some instruments employ two gratings in series to eliminate such errors.

A prism must be constructed of material which transmits light of the wavelength range desired. Glass is suitable for the visible and the near ultraviolet region. Quartz is generally employed

1. Hogness, T. R., Zscheile, F. P. and Sidwell, A. E., J. Phys. Chem., 41, 379 (1937).

for the ultraviolet region. Since quartz exhibits the property of double refraction, two pieces of quartz, one right-handed and one left-handed, must be used in the construction of the prism, or the light must be reflected and returned through the prism so that it passes through the prism in both directions. At least two surfaces of a prism must be very carefully polished flat. These requirements increase the cost of a prism. On the other hand, the resulting spectrum has only one order and there will be no overlapping of orders in the emerging beam. Since the prism surfaces are carefully polished, it is possible to predict the directions in which stray light will be reflected and to place absorbing baffles in the instrument to absorb such light. Prisms show greater dispersion in the short wavelength region of the spectrum than in the longer wavelength region; therefore the light will be purer for the same size exit slit in the short wavelength region. A grating, on the other hand, shows about the same dispersion throughout the entire spectrum.

Stray light can be detected by using as a light source some device which emits discontinuous radiation as, for example, a mercury arc. No light should pass through the monochromator when the wavelength setting is a few tenths of a millimicron from the wavelength of some line in the spectrum of the source.

A mercury arc or even a common fluorescent light serves as an excellent check on the wavelength scale readings. The mercury line at 546.1 mμ is especially suitable and can easily be detected using a fluorescent light bulb. A hydrogen discharge tube gives a fairly intense line at 656.3 mμ which is also useful in wavelength calibrations.

For checking the transmittance values registered by an instrument, the filters available from the National Bureau of Standards are useful. Several solutions have also been suggested for this purpose. Potassium chromate in 0.05 N potassium hydroxide was used by von Halban[2] and by Hogness, Zscheile, and Sidwell.[1] Potassium nitrate has been used by Scheibe.[3]

VISUAL SPECTROPHOTOMETERS

Although visual spectrophotometers are not widely used at present, a few are available and, therefore, a brief description of such devices is included at this point. The visual spectrophotometer is always so constructed that the light passing through the solvent can be decreased in intensity by definite measured amounts and thus can be made to match the intensity of the light passing through the solution. This is accomplished in various instruments by using two Nicol prisms, one of which can be rotated with respect to the other; by interposing neutral wedges in the beam; or by using rotating sectors, the size of the sector opening being variable. What has been said previously regarding the errors inherent in visual colorimetry due to the human eye apply here as well.

2. von Halban, H. and Siedentopf, K., Z. Physik. Chem., 100, 208 (1933).
3. Scheibe, G., Ber., 59, 2616 (1926).

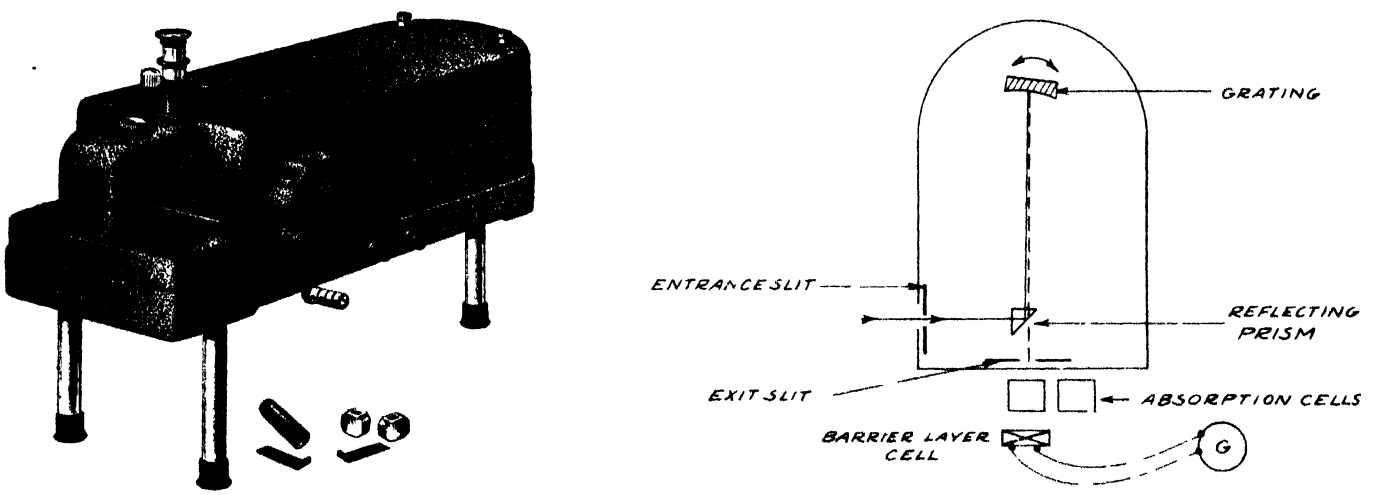
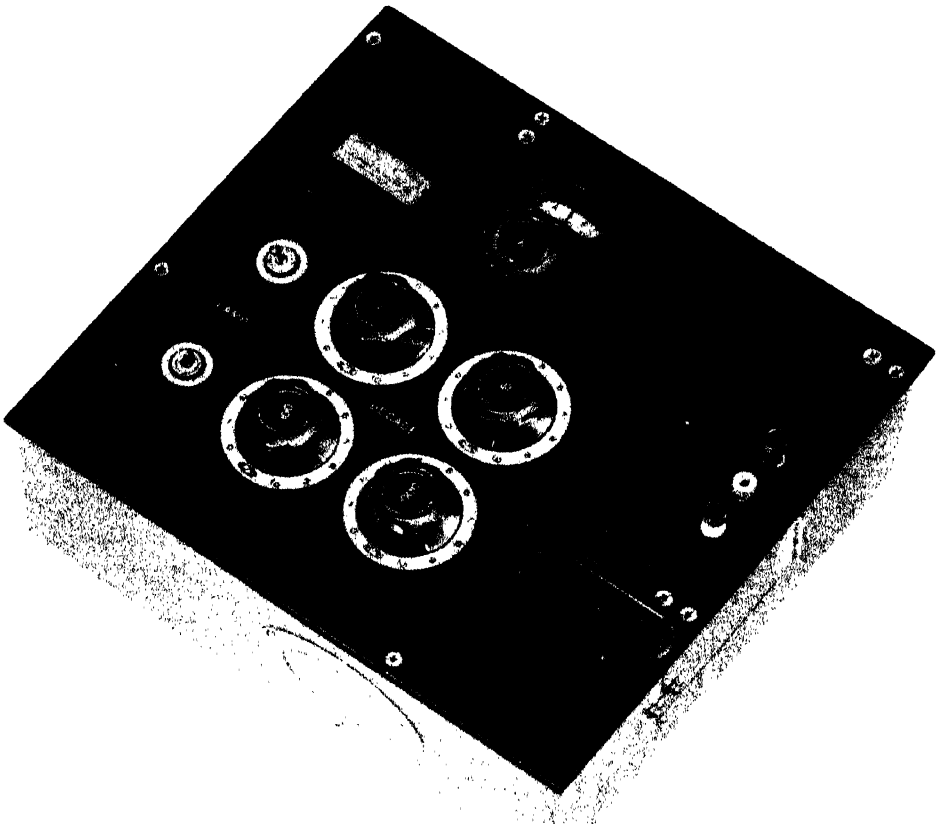


Fig. IV-1. Cenco-Sheard Spectrophotelometer (Courtesy of Central Scientific Co.)



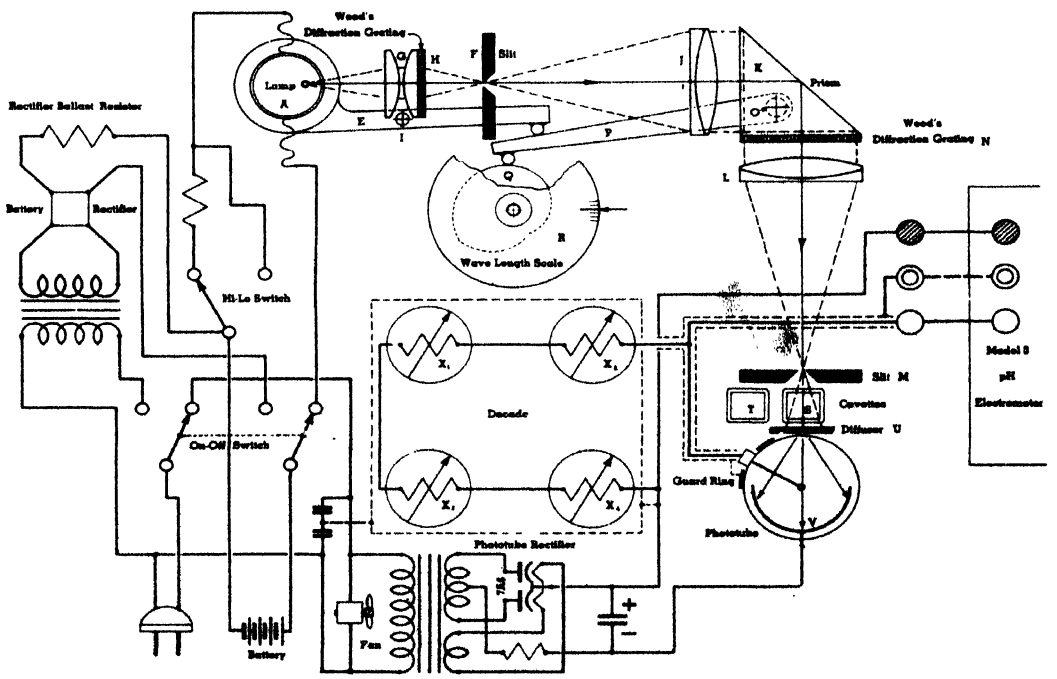


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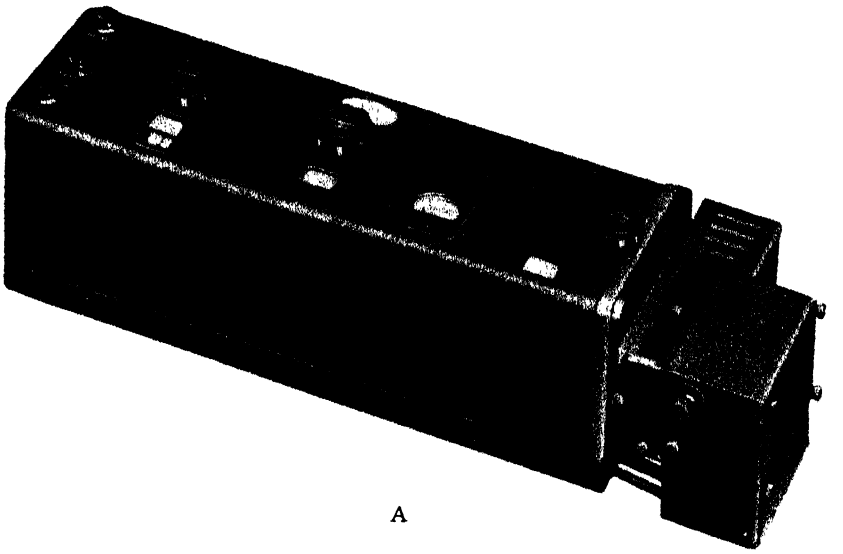
Fig. IV-2. Coleman Double Monochromator Spectrophotometer (Courtesy of Coleman Instruments,



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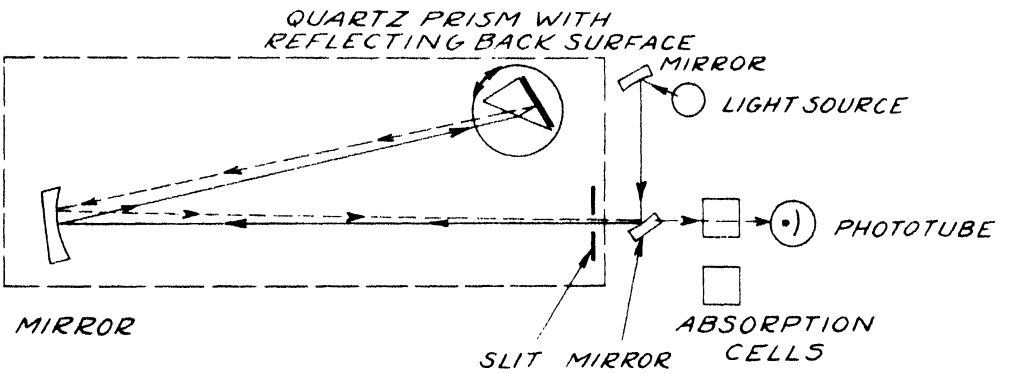

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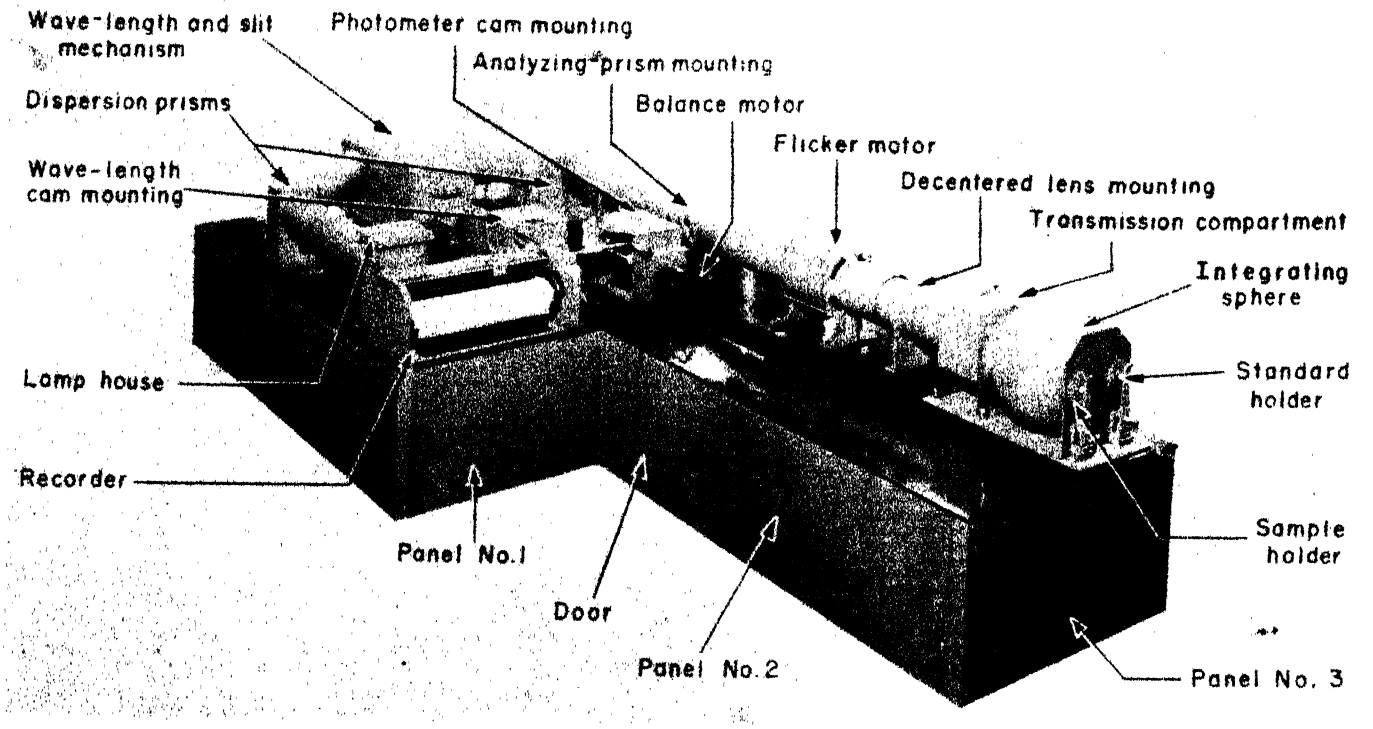
Fig. IV-3. Beckman Spectrophotometer (Courtesy of National Technical Laboratories)

PHOTOELECTRIC SPECTROPHOTOMETERS

Photoelectric spectrophotometers, like the corresponding filter photometers, may be divided into one-cell and two-cell instruments. They can be further subdivided, if desired, as to whether a grating or a prism is used in the monochromator and as to whether or not they are automatically recording.

Examples of several typical one-cell photoelectric spectrophotometers are shown in Figs. IV-1 to IV-3. The Beckman quartz spectrophotometer is probably the most widely used instrument at present and seems to be responsible for the great amount of work on absorption spectra which is currently appearing in the literature. The errors which occur in one-celled filter photometers will, of course, also appear in one-celled spectrophotometers. An instrument with a fixed light source rigidly mounted with the instrument is to be preferred.

Since the Cenco and the Coleman spectrophotometers use gratings, a few fixed slits serve to isolate bands of definite width. The Beckman instrument has a continuously variable slit. The wavelength range isolated by a given slit width on this instrument is also a function of the wavelength since a prism is used as the diffracting medium. The actual values of the "effective slit width" are determined from a graph furnished with the instrument. The ranges of the respective instruments are: Coleman, 350-1000 mμ; Cenco-Sheard, 325 (with special light source)-750 mμ; Beckman, 220-1000 mμ. In order to cover the range from 220 to 1000 mμ, the Beckman instrument employs two light sources - a hydrogen discharge bulb for the range 220 to 320 mμ and a tungsten auto headlight bulb for the range 320 to 1000 mμ. The hydrogen discharge bulb is operated from an electronically controlled



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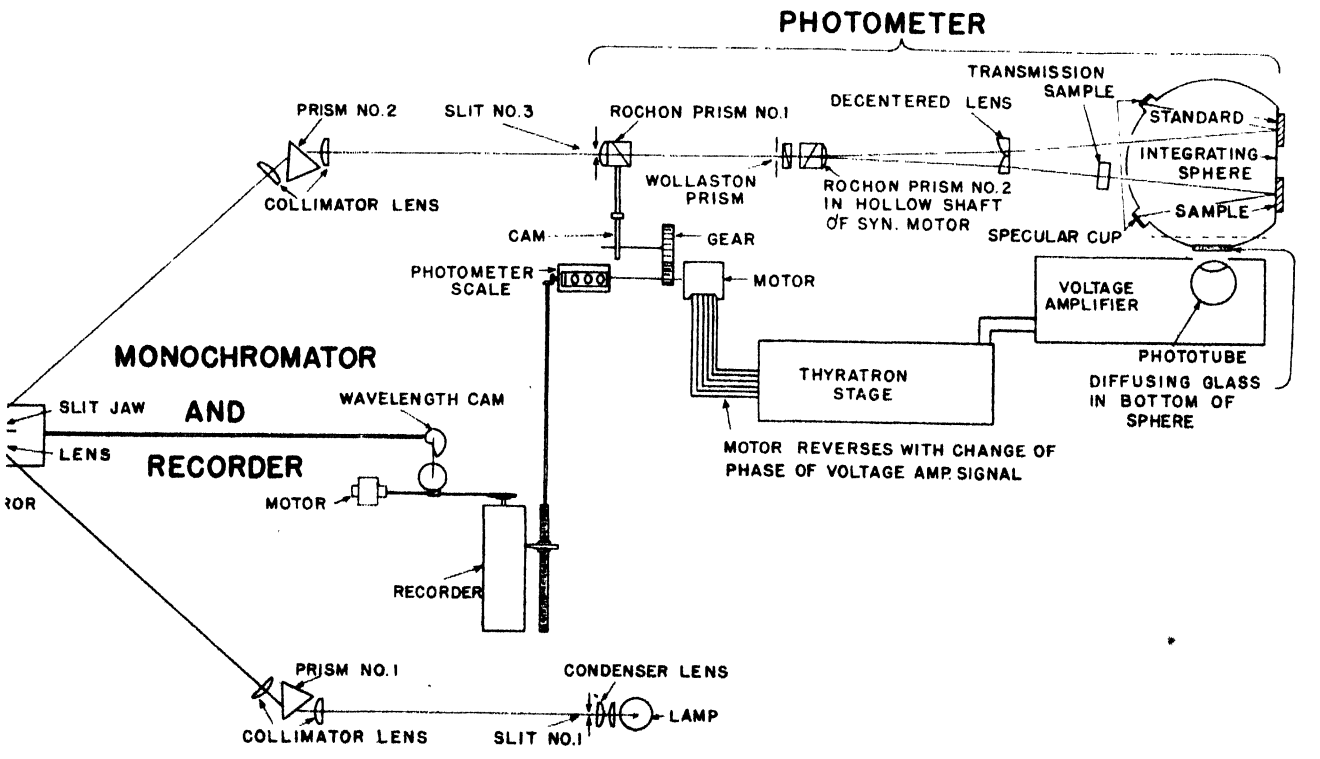


B

Fig. IV-4. G-E Recording Spectrophotometer (Courtesy of General Electric Company)

voltage supply, and the tungsten bulb is operated from a storage battery. The Coleman also uses a tungsten bulb operated from an 8-volt storage battery. The Cenco-Sheard instrument employs large projection-type tungsten filament bulbs operated from the A.C. power lines. Regulation is accomplished by constant-voltage and constant-current transformers.

The measuring cell in the Cenco-Sheard instrument is a barrier-layer cell and a galvanometer is used directly to measure the current output of the cell. The Coleman and the Beckman instruments employ vacuum photoemissive type cells, two different ones being required to cover the range of the Beckman instrument.

Several fine research instruments for special purposes or with exceptionally small effective slit widths are to be found described in the literature.[1] Several "null" type instruments, somewhat similar to the visual spectrophotometers, are also to be found in the literature.[2]

The General Electric photoelectric recording spectrophotometer, Fig. IV-4, is an excellent example of a two-cell recording instrument. The light emerging from the monochromator through slit No. 3 becomes polarized in passing through Rochon prism No. 1. The Wollaston prism is so set that the polarized beam from Rochon prism No. 1 is split into two beams, polarized at right angles to each other. These two beams pass through a second Rochon prism which is mounted at the center of a rotating motor. Thus the intensities of the two beams are alternately increased and decreased, one beam increasing in intensity as the other decreases, and vice versa. Now, if the transmission sample does not remove light from one beam, the intensity of the light in the integrating sphere will be constant. If the transmission sample absorbs light, a pulsating light intensity will be apparent in the sphere. This pulsating intensity will produce a pulsating current in the phototube. The output of the phototube is amplified by an A.C. amplifier and fed to the motor attached to prism No. 1 in such a manner that the motor will turn the prism to decrease the intensity of the upper beam until it matches that of the lower. A record is made of the position of this prism as a function of the wavelength and thus the absorption curve is obtained. The results are said to be more precise than those of the manual instruments and a complicated curve can be traced in a few minutes. The range is from 400 to 750 mμ, but a similar instrument with a range from 200 to 1000 mμ has been devised by Harrison.[4]

4. Harrison, G. H. and Bentley, E. P., J. Optical Soc. Am., 30, 290 (1940).

The determination of absorption curves by photographic means will be considered in a later chapter on the spectrograph.

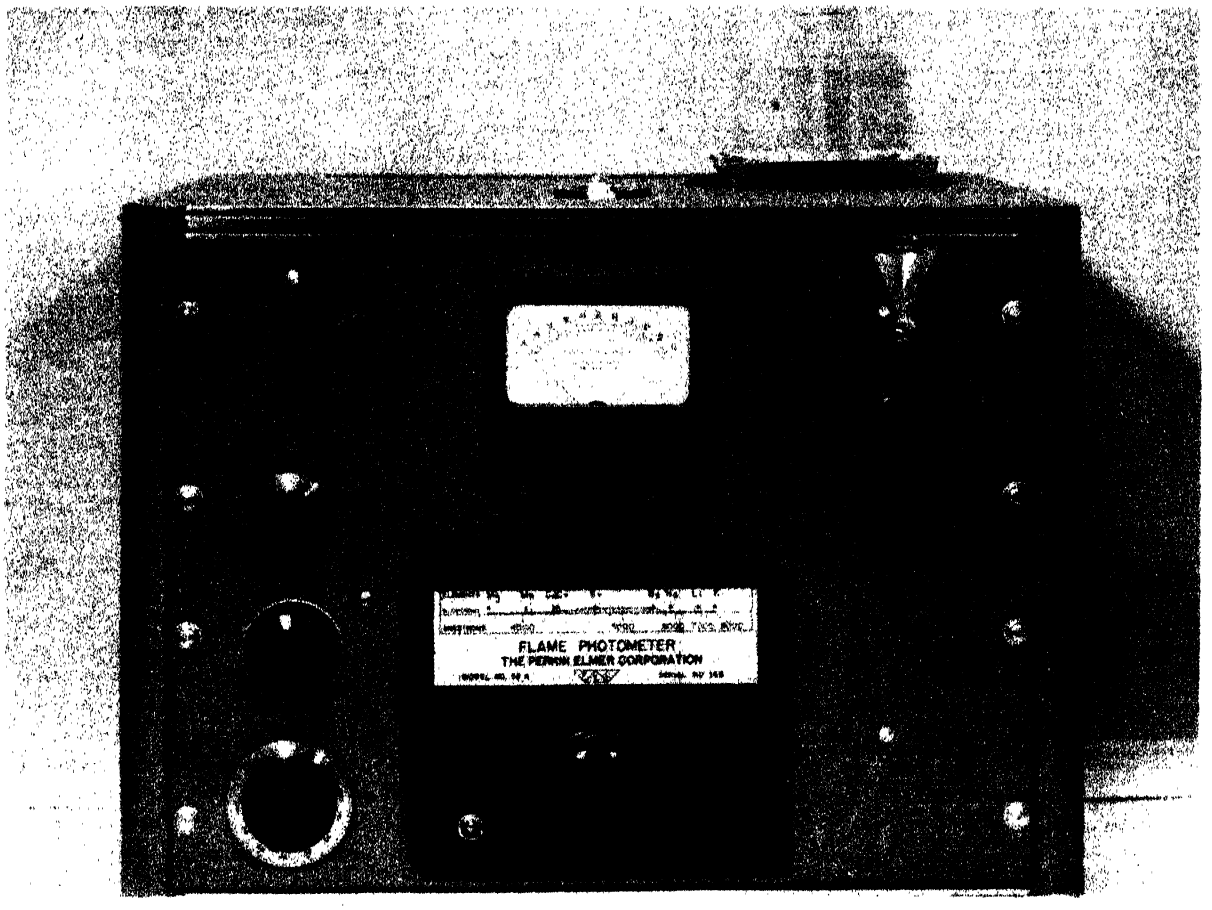
USES OF SPECTROPHOTOMETRIC DATA

Since the per cent transmittancy of a substance is determined by the spectrophotometer even more precisely than by a filter photometer, it is obvious that the spectrophotometer is an excellent device for determining the concentration of absorbing substances. Many instruments have scales reading directly in optical density. The purity of light available on a spectrophotometer is much better than that available from filters; therefore it is possible to determine the concentrations of components of mixtures more precisely and more readily by a spectrophotometer. Gases, liquids and solids can be measured. The amplifiers on most instruments can be adapted to make an automatic record of the concentration of one component of a flowing gas or solution. Since indicators show different absorptions in their acid and alkaline forms, it is possible to determine accurately the pH of solutions by measuring the concentration of the indicator in one or, preferably, both of its forms.

Space does not permit a discussion of the many physical and chemical properties of substances which can be determined by means of spectrophotometric measurements. Such properties as the ionization constants of weak acids and bases, the dissociation constants of complex ions, the nature of complex ions, the rates of reactions, and even much valuable information on the molecular structure of complicated compounds can be obtained from spectrophotometric data. The specification and analysis of color are of great importance in the paint and textile industries.

The usual conventions in plotting spectrophotometric data are to plot increasing values of the molecular extinction coefficient, ϵ, or log ϵ as ordinate against increasing values of frequency, in Fresnel units, or decreasing values of wavelength, in millimicrons, as abscissa.

The optical density, D (also called the extinction, E) or the specific extinction coefficient, k, or log k, are also sometimes plotted as increasing values on the ordinate. Occasionally percentage transmittancy values are used as ordinates, but this system does not show up the most interesting points, the absorption maxima, as well as the other methods. In all cases, the worker should report the concentration of the solutions used, the solvent employed, the slit widths em-



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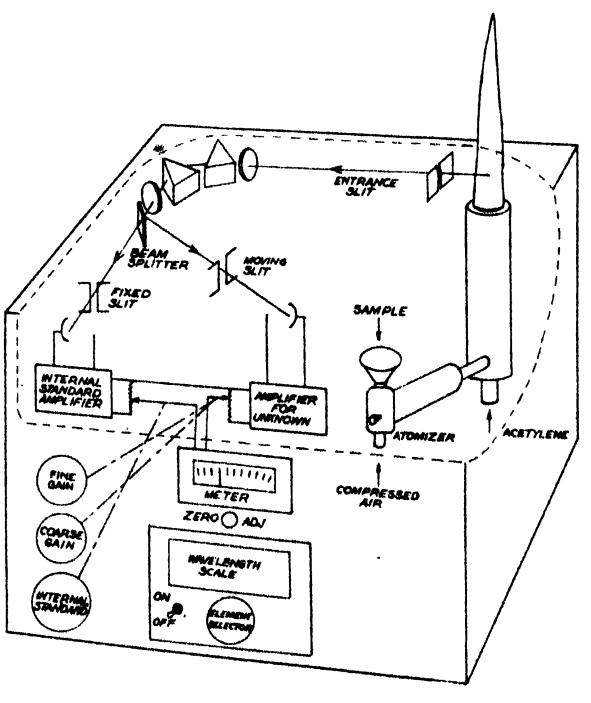
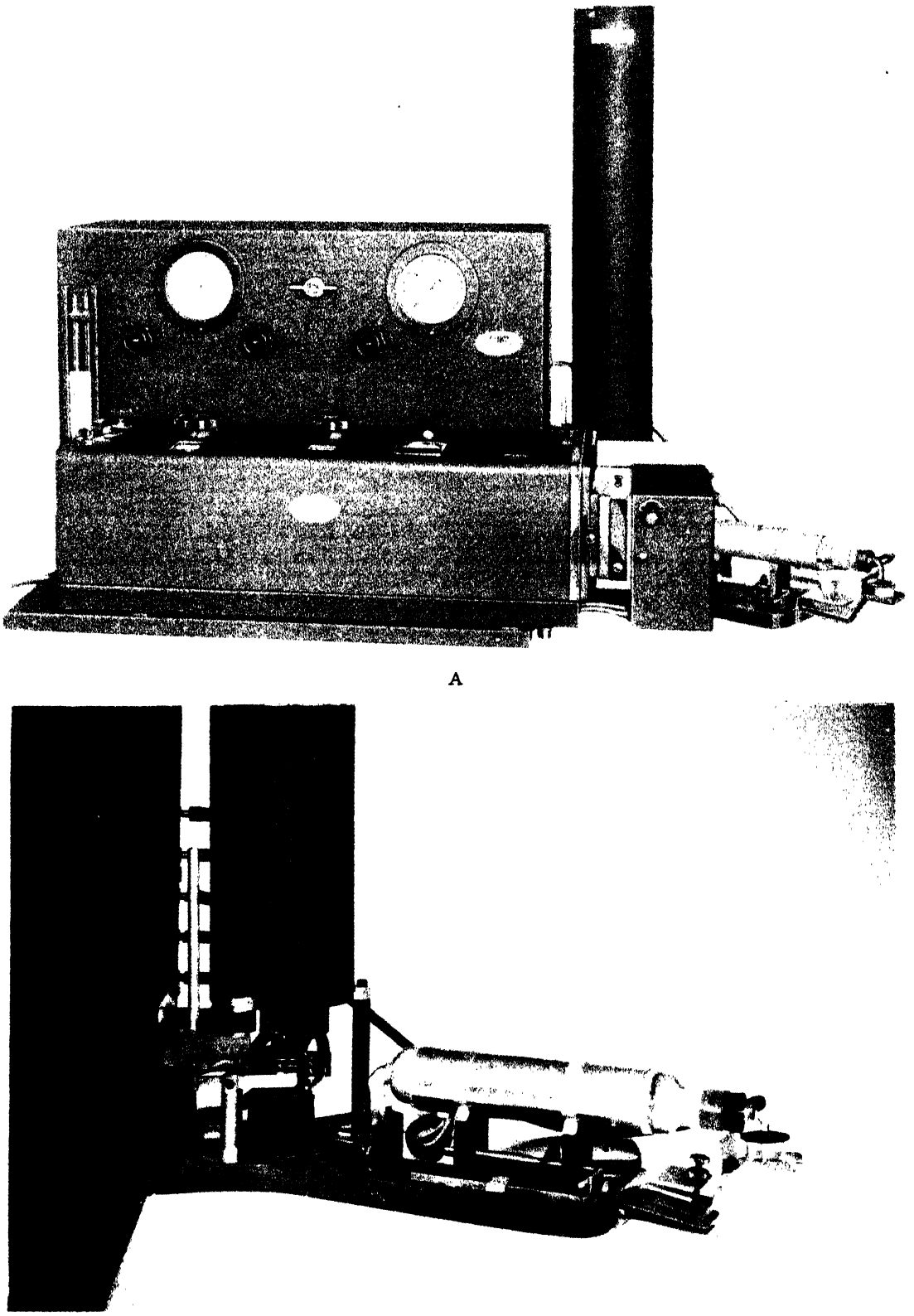


B

Fig. IV-5. Perkin-Elmer Flame Photometer (Courtesy Perkin-Elmer Corporation)



A

Fig. IV-6. Beckman flame photometer attachment with Beckman Spectrophotometer (Courtesy of National Technical Laboratories)

ployed, the make and model of the instrument, and any other pertinent information.

Water is a common solvent for many inorganic substances for spectrophotometric measurements. For organic substances "spectrographic" cyclohexane, ethyl alcohol, iso-octane, ethyl ether, and ethylacetate are frequently employed. Solvents should be especially purified for spectrophotometric work and should be free from suspended matter, bubbles, etc. It should be remembered that benzene is a frequent impurity in absolute ethyl alcohol and some other organic solvents.

The absorption bands of many substances are sharper and may show fine structure when measured in solvents of low dipole moment.

All absorption cells should be kept scrupulously clean and free from scratches. Cells should be cleaned with concentrated nitric acid or aqua regia rather than with dichromate solutions since the latter has a tendency to be adsorbed by the glass. The cells should be rinsed several times before drying. The cells should also be checked to see that they are equivalent by placing the same solution in both cells and taking several readings of the transmittancy values. One cell is usually reserved exclusively for the solvent during actual use.

FLAME PHOTOMETRY

The flame photometer is a rather recent development in the field of analytical instruments. The fundamental ideas involved are, however, not new. Actually a flame photometer is a device for measuring the intensity of the light emitted by elements when excited in a flame. A discussion of the flame as an excitation source is included in Chapter V.

Since only a relatively small amount of energy as compared to that in a spark or arc is available in the flame, the elements do not emit a large number of lines. This makes the isolation of the desired lines quite simple. The Perkin-Elmer flame photometer, shown in Fig. IV-5, uses two prisms to isolate the desired radiation. The Beckman flame photometer attachment, shown in Fig. IV-6, is made for use with the Beckman spectrophotometer, and, because of the greater resolution obtainable with spectrophotometers, it is capable of isolating lines that would interfere with each other in older filter instruments.

Most commercially-available flame photometers are one-cell instruments, that is, they measure the intensity of one line at a time. It is necessary, therefore, to keep the characteristics of the flame source constant throughout each series of measurements. This is accomplished by careful regulation of the air, gas, and oxygen pressures and rates of flow. The rate of addition of the sample to the flame is also controlled by the above regulation. For precise work the unknown is compared with standard samples of approximately the same concentration. Rough determinations can be made by keeping all variables constant and using a factor determined at some previous time to relate intensity to concentration.

The Perkin-Elmer instrument can be used for comparisons of the intensities of two lines at a time and thus the internal standard procedure described in Chapter V can be employed.

Qualitative analysis for elements in an unknown can be made by atomizing the solution into the burner and checking the light emitted for the wavelengths characteristic of the elements of interest. At least forty elements can be excited in a hot flame and can be determined qualitatively and quantitatively by a flame photometer. Determinations of the alkali metals are especially sensitive.

The flame photometer provides a rapid and relatively simple method for the analysis of a wide variety of mixtures. It will not replace the spectrograph in many cases but it does offer a quick, relatively inexpensive, method when only a few analyses of a kind are to be performed and, of course, for special situations. It has been suggested for the simultaneous analysis of mixtures of all the alkali metals, for determination of most of the rare earths in mixtures, the determination of traces of strontium and calcium in barium, silver in gold, copper in mercury, cobalt in nickel, etc.

Samples to be analyzed must be brought into solution. Nonaqueous solvents can be used if they are at least as volatile as water at room temperature. In the older models of the Beckman instrument, the samples are mixed with propyl or isopropyl alcohol (one volume of alcohol to five volumes of sample) in order to increase the rate of evaporation in the spray stream. Small, "dry" particles are thus fed into the flame. This gives a steadier flame and eliminates the necessity for cleaning between samples. In the newer model of the Beckman instrument the spray chamber is electrically heated and the addition of propyl alcohol is not necessary.

Table 1 lists the elements which can be determined with the Beckman Flame Photometer, the amounts easily detectable, and the amounts determinable to within 1%. It is claimed that, with careful work, one-fifth of the amounts listed can

TABLE 1. PRELIMINARY DATA ON THE BECKMAN FLAME PHOTOMETER
(By Courtesy of the National Technical Laboratories)

Element	Amount Easily Detectable ppm	Amount Easily Determinable to 1% %
Barium	2	0.05
Boron	5	0.1
Cadmium	500	
Calcium	0.3	0.005
Cesium	0.1	0.002
Chromium	2	0.03
Cobalt	5	0.1
Copper	2	0.04
Gold	70	1.0
Iron	10	0.2
Lead	300	
Lithium	0.05	0.001
Magnesium	10	0.2
Manganese	1	0.02
Mercury	70	1.
Nickel	15	0.3
Palladium	70	1.
Potassium	0.05	0.001
Rubidium	0.1	0.002
Ruthenium	30	0.5
Silver	2	0.04
Sodium	0.01	0.0002
Strontium	0.7	0.01
Thallium	1	0.02
Tin	500	

Also:

Bismuth	Lanthanum	Samarium
Dysprosium	Molybdenum	Scandium
Europium	Neodymium	Selenium
Gadolinium	Platinum	Tellurium
Gallium	Praseodymium	Yttrium
Indium	Rhodium	Zinc

usually be determined. Table 2 gives the wavelength of the lines used for the determination of the various elements and the relative intensity of each line. The relative intensity is defined as 100 divided by the number of parts per million of the element required to give a photometric response equal to 1/2% of the flame background.

INFRARED SPECTROPHOTOMETRY

The measurement of infrared absorption spectra of compounds is finding widespread use since stable, commercial, infrared spectrometers have become available. The infrared spectrophotometer is used for quantitative measurements of concentration and even for automatic control and recording. In addition, it is a valuable tool for detecting and identifying small amounts of impurities and for the elucidation of the structure of molecules.

Origin of Infrared Spectra

Infrared spectra arise from the different modes of vibration and rotation within a molecule. The pure rotational spectrum of molecules will occur at very long wavelengths, beyond about 25μ. At wavelengths shorter than this value, the light has sufficient energy to cause changes in the vibrational and, of course, also the rotational levels of the molecule.

According to the quantum theory, there are dis-

TABLE 2. WAVELENGTH AND RELATIVE INTENSITY OF LINES USEFUL FOR ANALYSIS
(By Courtesy of the National Technical Laboratories)

Element	Wave-Length	Relative Intensity	Element	Wave-Length	Relative Intensity	Element	Wave-Length	Relative Intensity
Co	238.9		Rh	359.6		Sr	460.7	150
Hg	253.6	0.15	Pd	363.5	1.5	Gd	461.4	
Au	267.6	1.5	Pb	364	0.1	Y	464.4	
Pb	283.3	0.1	Pb	368.5	0.2	Y	467.5	
Mg	285.2	10	Rh	369.1		B	473	5
In	303.9		Rh	369.6		Y	486.0	
Zn	307.2	0.01	Mg	370.8	10	B	495	10
Cu	324.8	50	Fe	372.0	7	Mn	510	10
In	325.6		Ru	372.7	3	Ba	520	20
Cd	326.1	0.15	Fe	373.6	10	B	521	15
Sn	326.2	0.2	Tl	377.6	80	Tl	535.0	
Cu	327.4	20	Mg	383	8	Mn	541	30
Ag	328.1	7	Fe	386.0	7	B	548	20
Na	330.2	7	Ga	403.3		Ba	550	20
Rh	332.3		Mn	403.4	100	Ca	556	200
Sn	333	0.2	K	404.6	7	Mn	561	70
Ag	338.3	50	Pb	405.8	0.3	La	563	
Rh	339.7		In	410.2		Na	589.3	10,000
Ni	341.5	3	Ga	417.2		Ca	603.5	100
Rh	343.5		Rb	420.2	3	Ca	626	300
B	345	0.3	Ca	422.7	100	Ca	650	100
Ni	349.3	2	La	438.4		Li	670.8	2,000
Co	350.2	20	La	443.3		La	714	
Ni	352.5	6	Rh	449.2		La	745	
Co	352.7	20	Gd	451.4		K	767	2,000
Rh	352.8		Sn	452.5	0.1	La	798	
Cr	357.9	70	B	454	2	Ba	850	50
Rh	358.3		Cs	455.5	0.7	Cs	852	1,000
						La	860	

crete energy levels, both rotational and vibrational, in which each molecule can exist. The energy of a rotational level is given by the equation

$$E = \frac{J(J+1)h^2}{8\pi^2 I} \qquad (1)$$

where J = quantum no. (1, 2, 3 . . . etc.);

h = Planck's constant;
I = moment of inertia.

If a molecule is raised from the energy state with quantum number J to that with quantum number J + 1, the energy involved will be

$$h\nu = \Delta E = E_{j+1} - E_j \qquad (2)$$

from which the frequency of the light absorbed can be shown to be

$$\nu = \frac{h(J+1)}{4\pi^2 I} \qquad (3)$$

The frequencies appearing can be seen to be nearly whole-number multiples of a fundamental frequency.

Unless the moment of inertia be very small as, for example, in the rotation of a linear molecule around the axis through the nuclei, the frequency involved is very low. Before a molecule can interact with radiant energy in this manner it is essential that it possess a dipole moment.

The more interesting region of the infrared, at least from the analytical standpoint, is the shorter wavelength region below 25μ where vibrational effects enter into the spectra. For an harmonic oscillator, the energy of each vibrational quantum state is given by the equation

$$E = (v + 1/2)\, hc\omega \qquad (4)$$

where v = quantum number (1, 2, 3, . . . etc.);
h = Planck's constant;
c = velocity of light;
ω = frequency (cm^{-1}).

If the motion is anharmonic a second term must be added to the above equation. For an harmonic oscillator the frequency, ω, is related to the force, f, binding the vibrating parts together and the reduced mass, μ, by the relationship:

$$2\pi\omega = \left(\frac{f}{\mu}\right)^{1/2} \qquad (5)$$

Thus the frequencies of vibration of a molecule are intimately related to the masses and the binding forces. This is the basis of the use of infrared spectra for the determination of the structure of molecules. For very simple molecules, such as water, and even for more complex but highly symmetrical molecules such as benzene, it is possible to subject the molecule to a thorough mathematical analysis and to predict thereby the frequencies of vibration. The strength of the binding forces must be known. For more complex molecules such a mathematical treatment is too involved and empirical methods of comparing the spectra with those of known compounds are resorted to.

The number of normal modes of vibration of a nonlinear molecule with more than 4 atoms is equal to 3 n - 6 where n is the number of atoms in the molecule. If the molecule is linear, the number of modes would be 3n - 5. Each normal mode of vibration can occur independent of the other modes and all can occur simultaneously.

In order for a vibration to appear in the infrared spectrum, that is, to be "infrared active," it is essential that there be a change in the electrical symmetry, or the dipole moment, of the system. Vibration of two similar atoms against each other, as, for example, in nitrogen or oxygen molecules, will not result in a change in the electrical symmetry of the molecule and, therefore, such molecules do not absorb in the infrared region.

Since both vibration and rotation occur simultaneously, each vibrational band will consist of three branches: One, the Q branch, in which J does not change as v changes; one, the P branch, in which J changes by -1 as v increases; and one, the R branch, in which J changes by +1 as v increases. Each vibrational band is, therefore, very complicated when completely resolved.

Qualitative Analysis.

Infrared absorption spectra can be used for the identification of pure substances or for the detection and identification of impurities. There are more applications in the organic field than in the inorganic field primarily because water, the chief solvent for inorganic compounds, absorbs strongly beyond about 1.5 μ. Inorganic compounds frequently have broad absorption bands, whereas organic compounds may show several narrower bands.

The infrared absorption spectrum of a compound acts as a sort of "fingerprint" for that compound. Thus, for the identification of substances in the pure state, it is necessary only to compare the spectrum of the unknown with the spectra of the various possible substances. Usually enough is known about the origin or the nature of an unknown substance so that a limited number of possible substances will be suggested to the analyst. When a match between spectra is obtained, identification is complete. The above procedure is especially useful in distinguishing between isomers.

The spectrum of a mixture of compounds is essentially that of the sum of the spectra of the individual components. Exceptions occur in cases where compound formation, association, dissociation, or polymerization takes place. In fact, shifts in infrared spectra from the predicted values are used as criteria for such behavior, for example, for hydrogen bonding,[5] etc.

In order to detect an impurity in a substance, comparison can be made of the spectrum of the suspected substance with that of a pure sample of the substance. Impurities will cause extra absorption bands to appear in the spectrum.

Identification of the impurities is accomplished by searching for compounds with bands in the same position as the extra bands appearing in the impure material. However, many of the bands of the impurity may be obscured by the bands of the main constituent and the remaining bands must serve for the identification. Catalogs of infrared absorption spectra, such as the one prepared by Barnes and co-workers,[6] are useful in identification of impurities. If the sample has been separated by fractional distillation, the impurity will probably have a boiling point similar to that of the main constituent and this fact may be a useful starting point in the search.

The most favorable case for successful analysis by means of infrared absorption spectra will occur when the impurity present possesses characteristic groupings or linkages not present in

5. Coggeshall, J. Am. Chem. Soc. 69, 1620 (1947).

6. Barnes, R. B., Gore, R. C., Liddell, U. and Williams, V. L., "Infra-red Spectroscopy," Reinhold Publishing Co., New York, 1944.

the main constituent. However, this is not a necessary criterion as is pointed out by Wright.[7] 1,2-Dibrompropane, although only a geometrical isomer of 1,3-dibrompropane, can be detected in concentrations as low as 0.3% in mixtures with the latter substance.

Since the individual bands occuring in the infrared spectrum are more or less characteristic of specific pairs or groups of atoms in the molecule, much information about the structure of a compound can be deduced from the spectrum. Above about 7 to 8 μ, the bands are likely to be due to vibrations in which all of the atoms take part. On the other hand, the bands below this wavelength are usually due to specific groupings and, therefore, this region is the most interesting. The position for a band due to a specific group shifts somewhat depending on the adjoining groups, but general regions can be assigned to many types of linkages (see Table 3).

TABLE 3. APPROXIMATE POSITION OF INFRARED ABSORPTION BANDS

Group	Frequency cm^{-1}	Group	Frequency cm^{-1}
C-H (aliphatic)	2700-3000	C≡N	2100-2250
C-H (aromatic)	3000-3100	C-Cl	600-700
N-H	3300-3370	C-Br	560
O-H (phenolic)	3700	C-I	500
O-H (phenolic, hydrogen bonding)	3300		
S-H	2570-2600		
C-O	1000-1050		
C=O (aldehyde)	1720-1740		
C=O (acids)	1650		
C-C	750-1100		
C=C	1620-1670		
C≡C	2100-2250		

The carbonyl band, C=O, serves as an excellent example of the influence of neighboring groups on the exact position of an infrared absorption band. Anhydrides usually show a double absorption band with one minimum between 1850 and 1800 cm^{-1}, and the second between 1800 to 1750 cm^{-1}. Ester carbonyls are generally in the region from 1750 to 1725 cm^{-1}. Aldehydes and ketones show bands between 1725 and 1690 cm^{-1} and acids from 1700 to 1670 cm^{-1}.

Quantitative Analysis

Since the absorption spectrum of a mixture is, in most cases, an additive function of the spectra of each component, it is possible to determine the concentration of the components. Theoretically the Bouguer-Beer law is applied in infrared determinations just as it is applied in ordinary visible or ultraviolet spectrophotometric determinations. From the spectra of pure materials using known or constant values of the cell thickness, the molecular or specific absorption coefficients are determined at selected wavelengths where each component has a strong absorption band and the other components have weak bands. The optical density of the unknown is determined at these selected frequencies. A series of linear equations can be set up and solved simultaneously for the desired concentrations. Unfortunately, this method is difficult to apply in many cases, and more empirical methods are often employed.

One of the chief difficulties encountered in quantitative infrared spectrophotometry is the presence of scattered light. Much of the energy from the sources employed in the spectrophotometers lies in the short-wavelength region and such light is strongly scattered. The energy at 1.5 μ may be as much as 100 times as great as that in the 10 μ region. Presence of scattered light makes the direct application of the Bouguer Beer equation inaccurate, especially at high values of the optical density.

Since the energy available in the useful wavelength range is quite small, it is necessary to use rather wide slits in the infrared spectrophotometers. The absorption of the compounds being investigated may have a width at half of the maximum optical density (the "half-width" of the band) which is comparable to the effective width of the slit. A very slight shift of the wavelength setting of the spectrophotometer would cause a considerable change in the apparent value of the specific extinction coefficient. Therefore it is not practical for the specific extinction coeffi-

7. Wright, Norman, Ind. Eng. Chem., Anal. Ed., 13, 1 (1941).

cients for a compound to be determined by one spectroscopist and be used by another worker on another instrument. Each worker must determine the values of k for each compound at definitely reproducible wavelength settings of his instrument.

If the given instrument can be made to reproduce the wavelength setting and the spectral slit width, a working curve of optical density versus concentration can be prepared. Otherwise it is necessary to use a comparison method of the unknown with knowns. Several empirical methods of calculation are to be found described in the literature.[8]

It is important to pick the proper thickness of cell in order to minimize errors. Differentiation of the Bouguer-Beer relationship shows that $\frac{1}{c}\frac{dc}{dT}$ is a minimum where $T = e^{-1}$ or at 37%. Thus at this value of T, errors in measurement of T will have the least effect on the concentration value. The sample thickness should be chosen so that the transmittancy, T, lies between about 25% and 50%. For most liquids this will represent a very thin layer, 0.03 to 1.0 mm., since infrared absorption bands are generally quite intense. Working with such small dimensions makes the problem of repeating the thickness difficult. The usual procedure is to keep the same cell without change throughout a series of determinations. Carbon tetrachloride and carbon disulfide are common solvents since they are quite transparent in the infrared region.

Gases are especially easy to measure in the infrared region because the concentration is readily controlled by varying the pressure. Furthermore, gases are much freer from intermolecular effects than solid or liquid samples. Gas cells may range from 1 to 20 cm. in length.

Applications

The most common type of analysis if probably the determination of a small amount of a known impurity in a given compound or mixture. If sufficient accuracy in reproducing the frequency settings, the cell thicknesses, the slit widths, and the intensity of the source can be obtained, then a working curve of transmittancy or optical density may be plotted. Wavelengths are chosen at which the component to be determined absorbs strongly and the other material either does not absorb or absorbs weakly.

For multicomponent mixtures, working curves can be employed when wavelengths can be found at which each component absorbs strongly and the other components do not absorb. In cases where more than the desired components show absorption at all usable wavelengths, simultaneous equations must be employed for the solution. The procedures become quite complicated.

The petroleum refining industry has been a large user of the infrared absorption procedures. Preliminary separations are almost always made by fractional distillation, but the analysis of each cut is greatly simplified by infrared and other methods.

In the industrial plant, spectrophotometers which can be set at fixed frequencies may be used to continuously record the composition of a stream of material. Automatic control can also be achieved by using suitable relays.

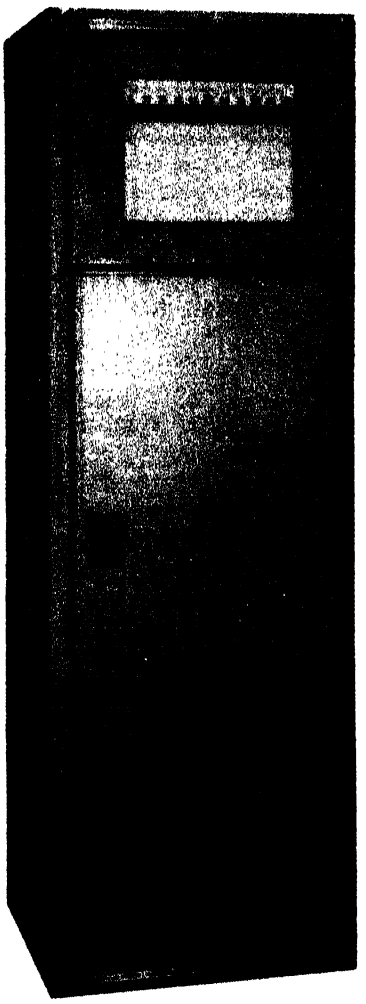
There are even methods which require no spectrometer, but only a source of infrared radiation and some suitable measuring device. This would be the case when some material which absorbs strongly in the infrared were to be measured in a mixture in which the other components did not absorb. A recent device of interest is the infrared gas analyzer made by Baird Associates (see Fig. IV-7). Radiation from the source is reflected by the mirrors through the box containing the gas to be analyzed. All radiation absorbed by the gas component which is to be determined is removed from one beam by the selective filter in the filter cell. This filter can conveniently be a high concentration of the component being determined. Radiation falling on the bolometer arm in this beam will not be affected by the desired component and thus serves as a standard. The compensation cell does not contain a filter gas, is not selective, and is placed in the second beam merely to maintain optical symmetry. Variations in the concentration of the desired component will affect the radiation falling on the second arm of the bolometer. Thus a comparison of the two beams yields a measure of the concentration of the desired component.

Instruments

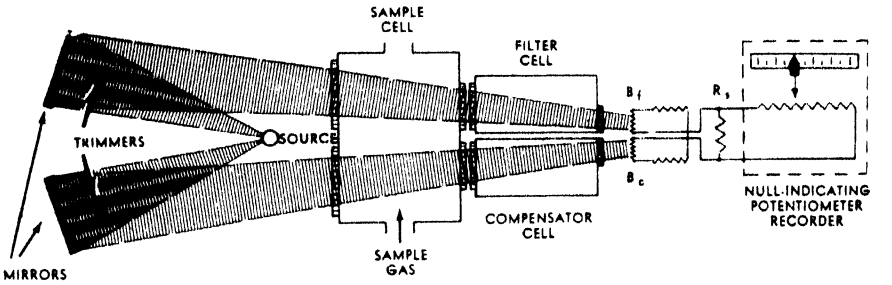
For measurements in the infrared region, at least beyond 3 or 4μ, several changes in the construction of ordinary spectrophotometers are necessary. These changes are due primarily to the facts that many substances, such as glass and quartz, absorb in the infrared region of the spectrum and that photocells do not respond in this region.

Most infrared spectrophotometers employ front-surface mirrors instead of lenses. This eliminates the necessity for light to pass

8, Fred and Porsschi, Ind. Eng. Chem., Anal. Ed., 18, 603 (1946), Lee, ibid, 18, 659 (1946). Seyfried and Hastings, ibid, 19, 298 (1947).



A



B

Fig. IV-7. Baird Associates Recording Infrared Gas Analyzer (Courtesy of Baird Associates Inc.)

through glass, quartz, or similar material. Furthermore, it would be difficult or impossible to make lenses which would bring light rays of the widely varying wavelengths in the infrared region to focus at one point. Occasionally a rough salt lens will be found in an infrared spectrophotometer, but such lenses are usually not essential optical components. Parabolic mirrors bring light of all wavelengths to focus at one point. Reflection from most metallic surfaces is generally very efficient in the infrared region.

Both gratings and prisms can be used for diffracting the light, but prisms seem to be more common, perhaps because energy in the infrared region is at a premium and none can be wasted in higher order spectra. The materials which are found most suitable in the infrared region are listed in Table 4 along with some of the important properties of each material. Large blanks of single crystals of most of these substances are available from the Harshaw Chemical Company, Cleveland, Ohio.

TABLE 4. PRISM AND LENS MATERIALS FOR INFRARED SPECTROSCOPY

Material	Range of Transmission	Most Suitable Region in Infrared
Quartz	0.18-3.5μ	0.80- 3.5μ
LiF	0.11-6	1 - 5
CaF_2	0.12-8.5	3 - 8.5
NaCl	0.20-15	8 -15
KBr	0.21-23	19 -28

Since most of these materials are soluble in water, the instruments must be carefully protected from high relative humidities. Carbon dioxide and water vapor also show many absorption bands in the infrared region.

Salt plates are cleaved, when reduction in thickness is required, and ground on "Speed-Wet" paper below saturated solutions of salt, then on dry "Speed-Wet" paper. Polishing is accomplished by grinding on glass laps with Norton

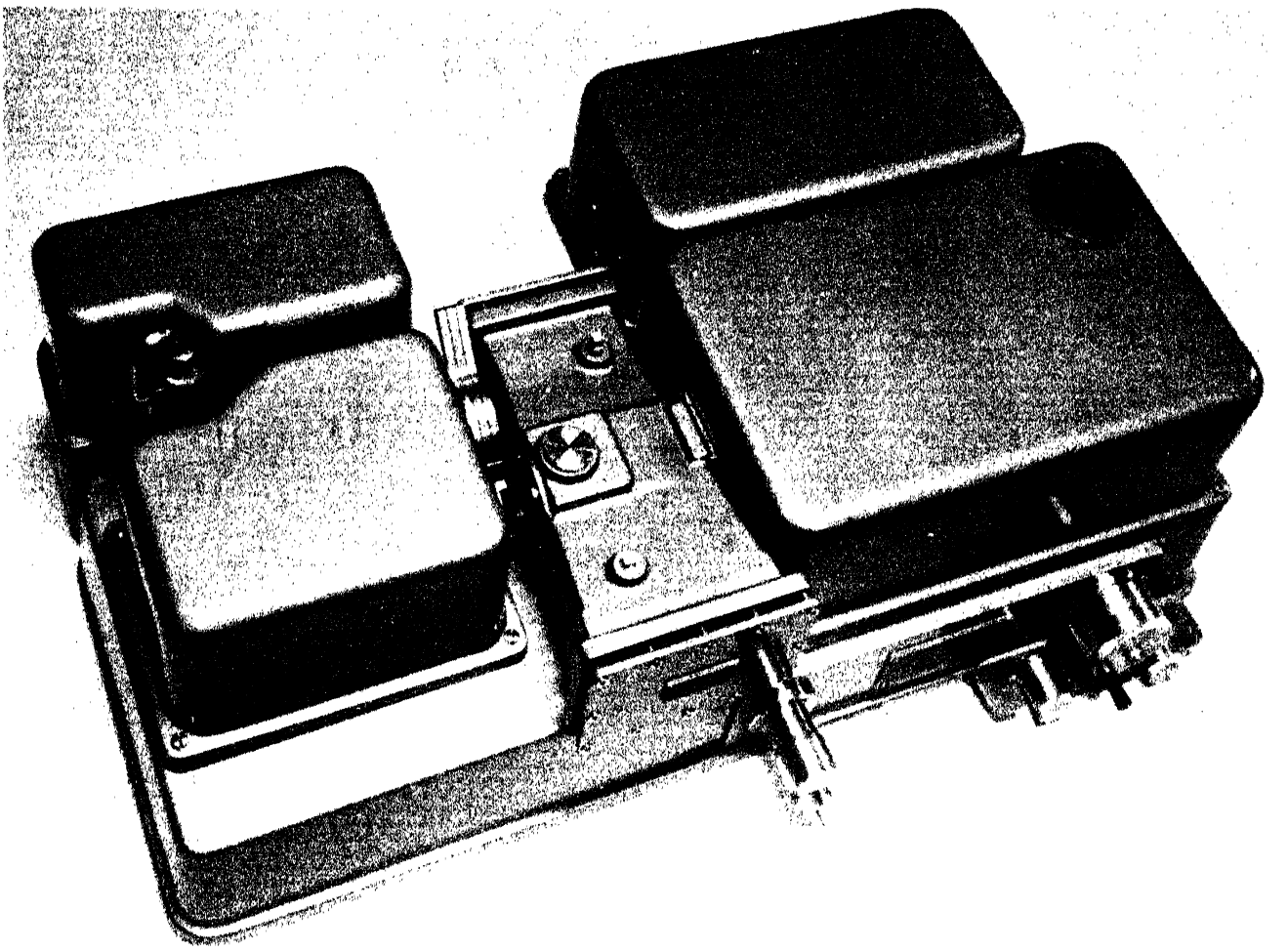


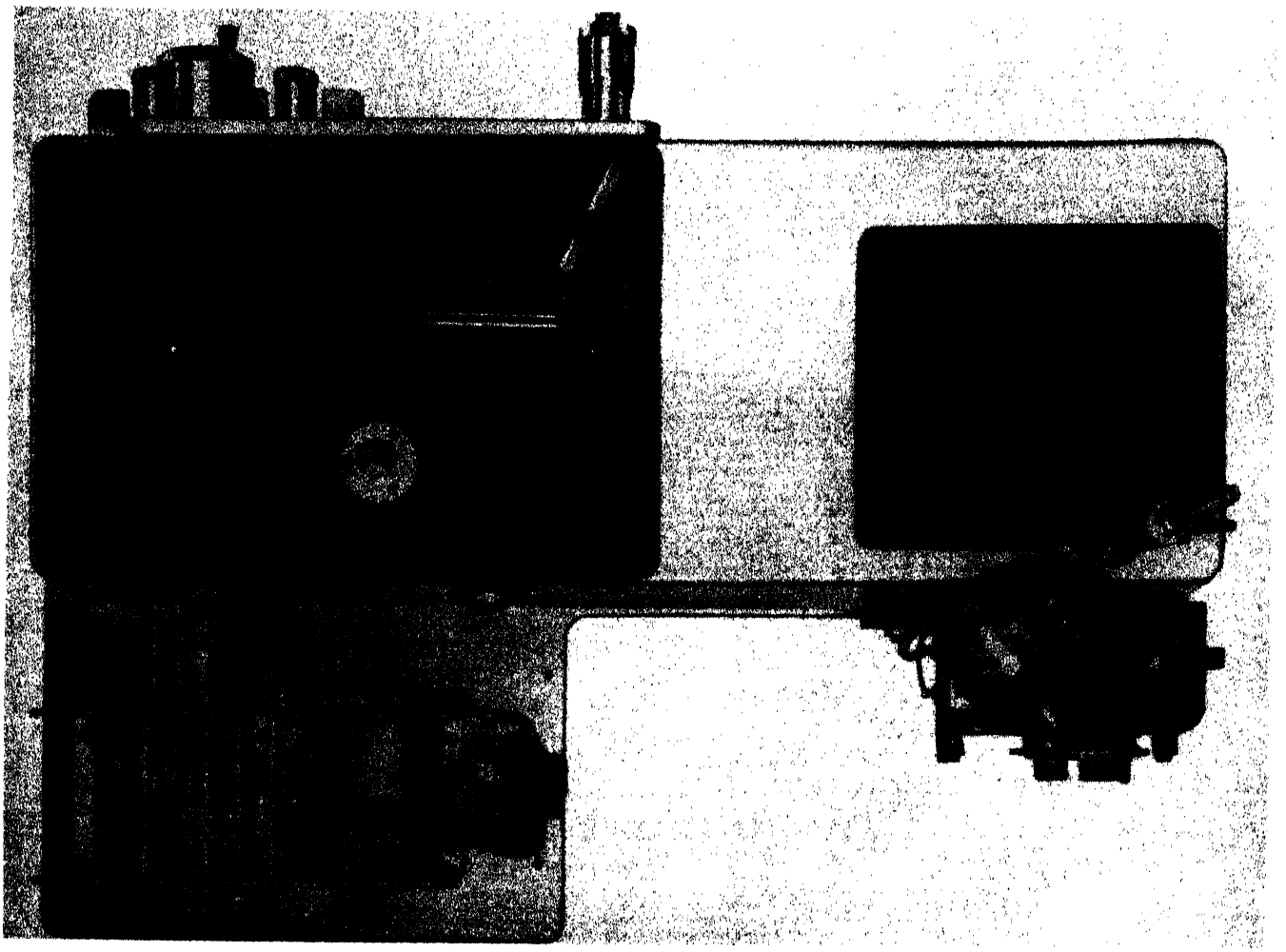
Fig. IV-8. Perkin-Elmer Recording Infrared Spectrophotometer, Model 12-C (Courtesy Perkin-Elmer Corporation)

Crystalon as abrasive and absolute alcohol as wetting agent and finally on broadcloth with "gold" rouge wet with absolute alcohol. Care should be taken never to breathe upon polished salt windows and never to touch them with the bare fingers. Use rubber gloves or finger cots and always hold the plate below, not above, the hand. Salt windows are sealed in place with lead gaskets. The gaskets are moistened with mercury and the window clamped in place. In time, the mercury amalgamates with the lead and the whole expands somewhat to make a tight seal.

The light source for an infrared spectrophotometer is a Nernst glower or a Globar. For the characteristics of such sources, see the brief discussion in Chapter II.

The receiving element for the infrared radiation must be a thermocouple, bolometer, or thermistor since photocells are not sensitive in this region of the spectrum. Indeed, the thermoelectric element chosen must be extremely sensitive since the average energy in the dispersed beam is very small. It has been calculated that a thermocouple must be capable of detecting differences of 5×10^{-5}°C. in order that the precision of measurement of the energy be about 0.5%. Small changes in ambient temperature can be minimized by using a two junction couple in series opposition, only one of the hot junctions being illuminated by the radiation being measured. The elements are further enclosed in a highly evacuated container. For further details of the various receiving elements, see the discussion in Chapter II.

The resistance of thermistors, bolometers, and thermocouples is low and amplification of the output is difficult. A photo-relay amplifier can be employed. A focused beam from a headlight bulb is reflected from the primary galvanometer, which is motivated by the thermoelement, onto the edge of a barrier layer cell. A small deflection of the galvanometer increases



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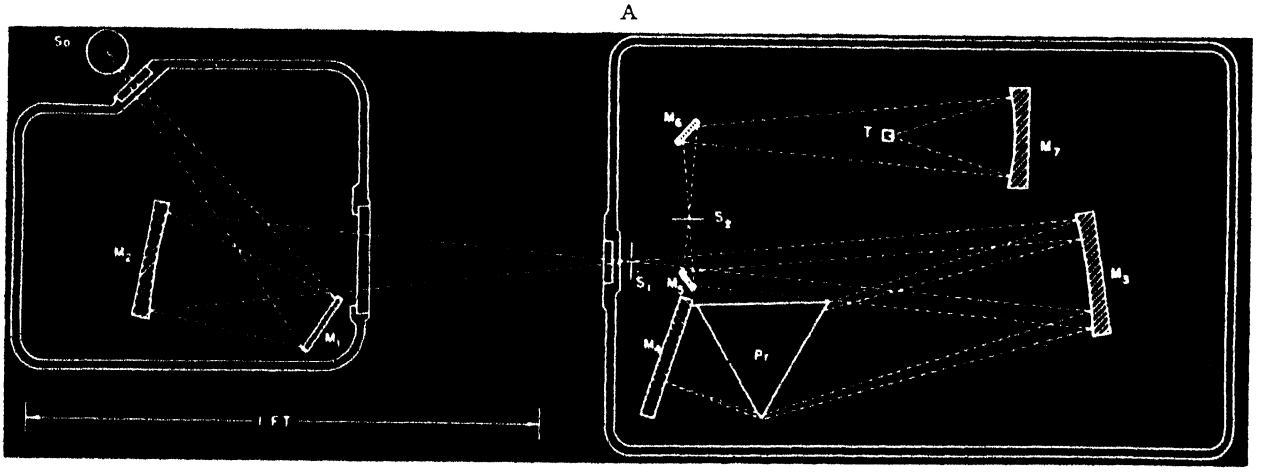


B

Fig. IV-9. Perkin-Elmer Recording Infrared Spectrophotometer, Model 12-C, schematic optical path. (Courtesy Perkin-Elmer Corporation). S, Globar source. G, rotating sector shutter. M_1 . . . M_7, mirrors. S_1, entrance slit. S_2, exit slit. Pr, prism. B, slit micrometer control. A, wavelength drive. T, vacuum thermocouple. P, pulsing circuit for producing fiduciary wavelength marks.

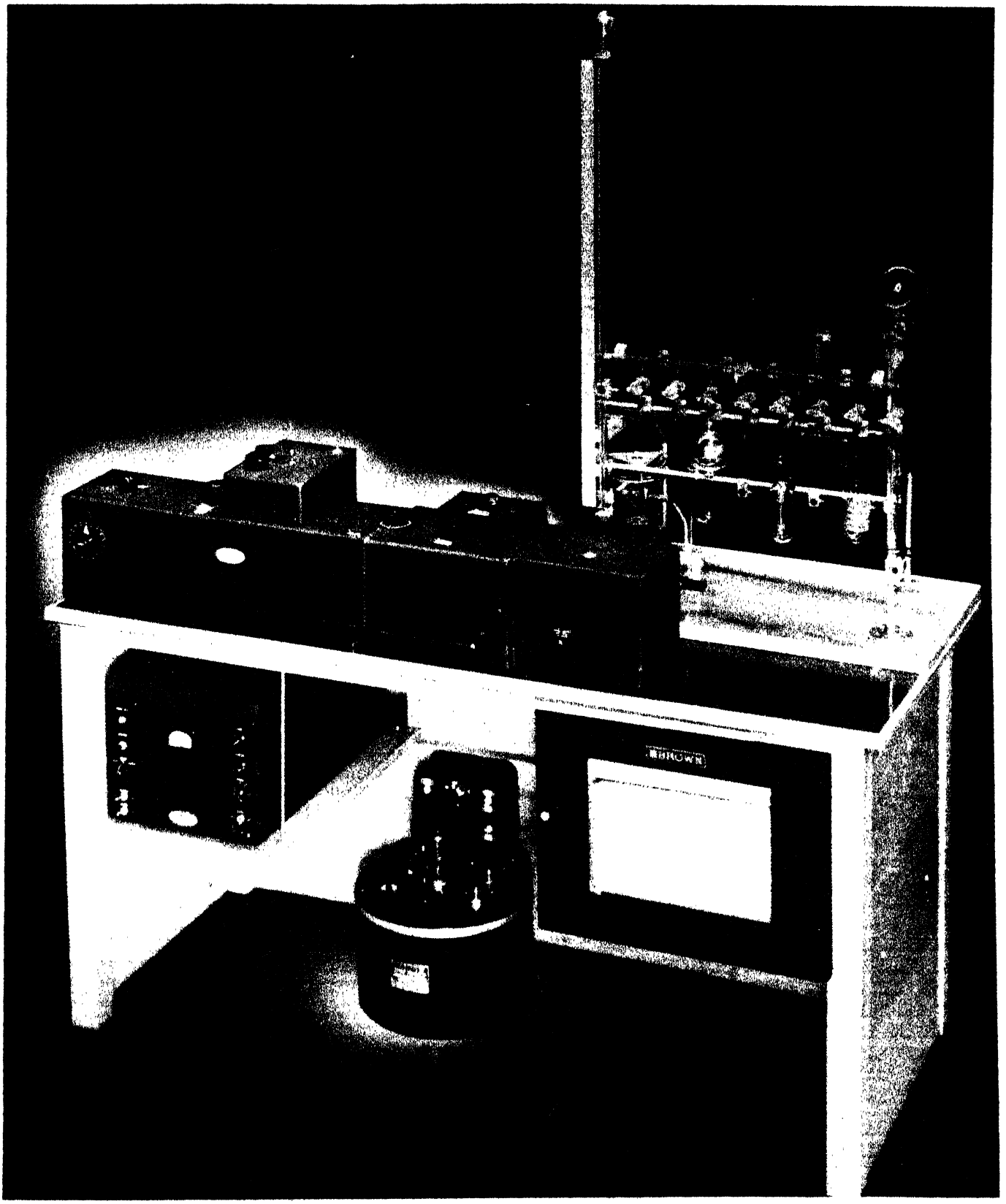


Fig. IV-10. Beckman Infrared Spectrophotometer, Model IR-2 (Courtesy of National Technical Laboratories)

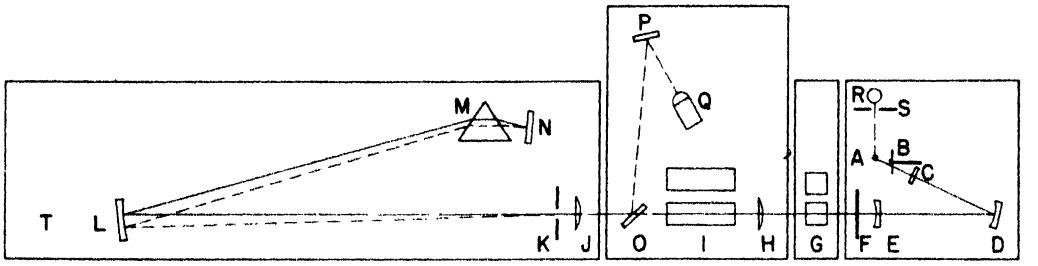


Fig. IV-11. Beckman Infrared Spectrophotometer, Model IR-2, schematic optical path. A, Nernst glower. B, rotating shutter. C, rock salt window. D, mirror. E, salt lens. F, filter slide and shutter. G, absorption cells for liquids. H, salt lens. I, gas absorption cells. J, salt lens. K, slits. L, mirror. M, prism. N, O, P, mirrors. Q, receiver. R, phototube to monitor source. S, light gate. T, position of turret-stop mechanism.

the illumination of the barrier layer cell and proportionally increases the current which is then fed into the recording galvanometer.

More recently the output from the thermosensitive elements have been amplified in a different and more satisfactory manner. The light entering the instrument is first chopped by a rotating shutter at a rate of 10 times per second or so. The light falling on the element is thus pulsating and a pulsating output is obtained. The element is then coupled to an A.C. thermionic amplifier by means of a condenser or transformer. The pulsating current is easily amplified and can eventually be recorded by a commercial recording potentiometer. Since any light which falls continuously on the receiver will produce only a constant D.C. output and will not be amplified, the errors caused by stray light and other constant energy effects tend to be eliminated. Above 9 μ a glass shutter is used to chop the light beam, thus permitting the short wavelength radiation to pass into the monochromator all of the time. This short wavelength radiation accounts for most of the stray light.

A turret mechanism is usually provided so that wavelength settings can be reproduced more accurately than by the wavelength scale. These turret mechanisms are an advantage when the same material is to be determined at irregular intervals.

The optical diagrams of the Perkin-Elmer and of the Beckman Infrared Spectrophotometers are shown in Figs. IV-8 to IV-11. The two-beam instrument manufactured by Baird Associates is shown in Figs. IV-12. In the Baird instrument, the reference beam and the beam through the absorption cell alternately strike the bolometer. When the beams are not of the same intensity, the bolometer will furnish a pulsating output which is amplified and used to drive a comb-shaped device to reduce the intensity of the reference beam.

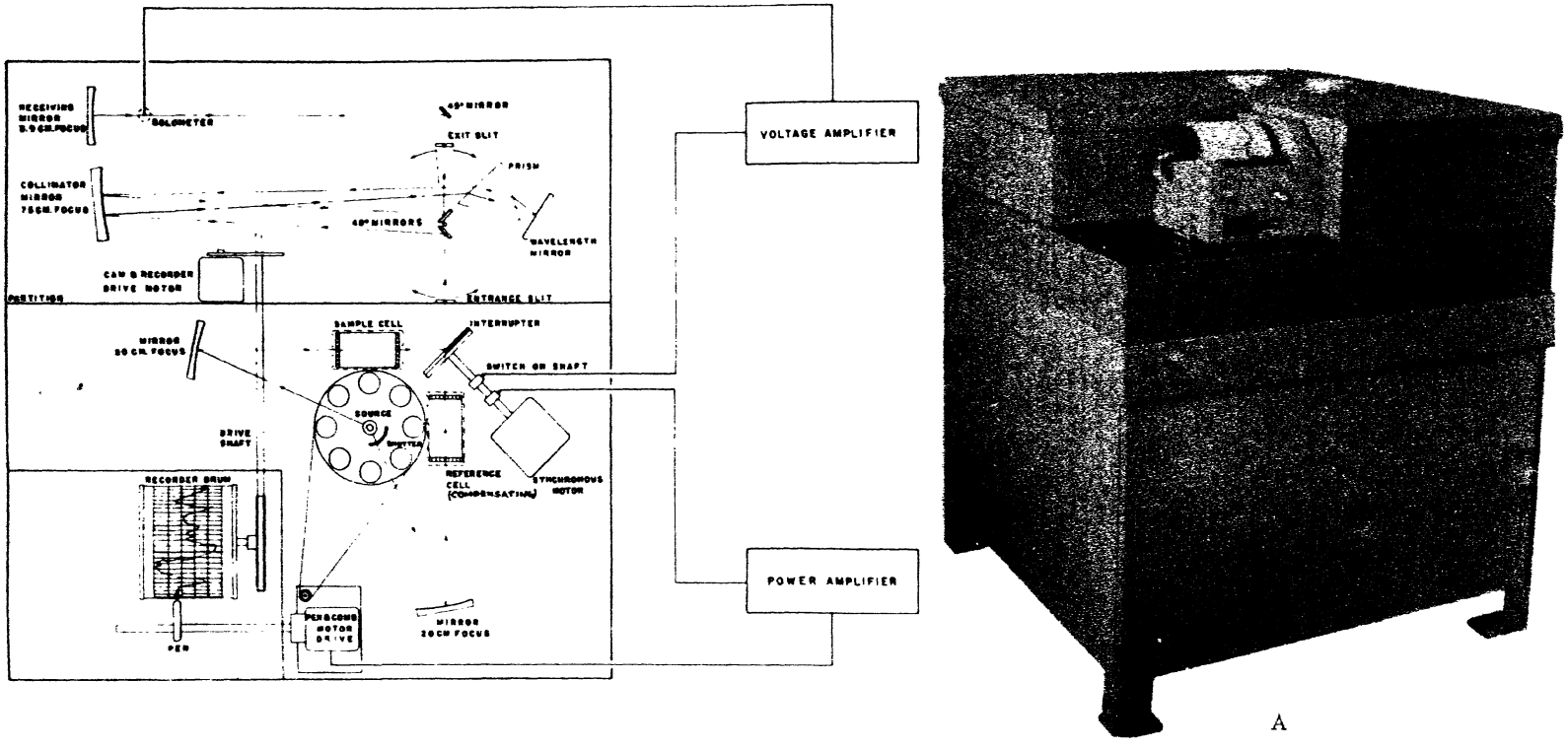
LABORATORY WORK WITH SPECTROPHOTOMETERS

Operating Instructions for Beckman Spectrophotometers[9]

Batteries (Instructor Only). Any good automobile battery may be used, but, to insure tube stability, it is preferable to use a high-capacity battery or two ordinary automobile batteries connected in parallel. Securely attach the battery clamps marked -, +2, and +6 to the corresponding voltage terminals of the storage battery. It is not necessary to parallel the 2-volt terminals. Batteries should test above 1250 specific gravity at all times. The dry cell batteries (six Burgess #5540) are mounted beneath the monochromator case. They are connected in the amplifier circuits and should give several months of service. Exhaustion is indicated by failure to make needle cross the meter scale when rotating sensitivity and dark-current knobs.

2. Absorption Cells and Holder. It is recommended that the cell holder be used with the corner springs toward the phototubes and that it be removed from the compartment for loading and unloading. It is also recommended that the front position in the holder be used for the cell containing the solvent. One of the ground glass sides of each cell should be marked to insure that each cell is used always in the same position in holder. The cells may be calibrated by filling them with

9. Adapted, by permission from the directions furnished by the makers, the National Technical Laboratories, South Pasadena, Calif.



A

B

Fig. IV-12. Baird Associates Two-Beam Infrared Spectrophotometer.

distilled water - do not compare empty cells.

Before use, the cells should be thoroughly cleaned, using distilled water or other suitable solvent. Do not use hot concentrated acids, which might spoil the polished surfaces. Remove cells from holder for cleaning and filling. Before replacing them, carefully wipe the outside surfaces. Use Corex cells (serial numbers start with C) for measurements above 320 mμ and silica cells (serial numbers start with S) below 320 mμ.

3. Place holder containing filled cells on the slide-in compartment and make certain it is seated properly, with knob pushed IN. Replace cell compartment cover. Each cell may be moved into the light beam by pulling the slide knob to the stop.

4. Phototube Selection. The proper phototube to use is determined by the spectral range to be investigated. The red-sensitive phototube for use above 625 mμ is in position when the knob on the phototube housing is pushed IN. The blue sensitive, or ultraviolet-sensitive, phototube for use below 625 mμ is in position when the knob is pulled OUT as far as possible. The model D spectrophotometer is equipped with blue-sensitive and red-sensitive phototubes, for measurements in the range 320 to 1000 mμ. The model DU is equipped with ultraviolet-sensitive and red-sensitive phototubes, for the range 220 to 1000 mμ - below 320 the hydrogen discharge tube must be used in place of the tungsten lamp. The two electronic tubes of the amplifier circuit are mounted in the phototube compartment.

5. Filter Slide. The filter slide is located between the exit slit and cell compartment and is operated by means of the knob on front end. The front position, knob pushed IN is blank and is used for measurements in the range 400 to 1000 mμ - also with the hydrogen tube. The second position contains a red-purple filter and is used in the range 400 to 320, with tungsten lamp. The third position is blank and may be fitted with special filter or lens for unusual applications.

6. Sensitivity Control. For best performance it is suggested that the sensitivity knob be used 1 to 3 turns from its clockwise limit. This insures maximum accuracy on the per cent transmittance measuring circuit and requires comparatively wide slit openings. If it is desired to employ narrow slit openings, the sensitivity knob may be used near its counterclockwise limit. At the former limit the accuracy to which the per cent transmittance slide wire can be set is only 10% as compared to that with sensitivity knob at clockwise limit.

7. Nominal Band Width. Fig. IV-13 gives the "effective band width vs. wavelength" relationship, from which the required slit opening for a given band width can be determined, for any wavelength of interest. If it is desired to make measurements with the very minimum band width, the instrument switch may be used in the "0.1" position and the slide wire set to 100% transmittance for balancing with solvent solution in the light beam - sensitivity knob should be used near its counterclockwise limit. In this procedure the transmittance scale is read 0 to 110% - not 0 to 11%.

8. Selector Switch. The main instrument switch has four positions - Off, Check, 1.0, 0.1. In the "Off" position all circuits within the monochromator and those to the phototube compartment are disconnected. (Separate switches are provided for tungsten lamp and hydrogen discharge tube.) The "Check" position provides a very convenient means of adjusting the instrument for 100% transmittance on the solvent without having to set the transmittance scale to 100% - the slide-wire being disconnected. Measurements on the unknown solutions are usually made with the switch on 1.0 - the scale being read to 0 - 100% transmittance, or 0 to 2.0 density. Position 0.1 is used for samples having less than 10% transmittance the scale being read 0 to 11% transmittance and 1.0 to 3.0 density - a tenfold increase in scale sensitivity. The 0.1 position also permits measurements with extremely narrow spectral band widths - paragraph 6, above.

9. Operation. Rotate wavelength knob until desired scale value is shown under hairline. Select proper phototube and filter if desired. Set selector switch to CHECK. Turn shutter switch OFF. Turn lamp switch ON. Rotate dark-current knob to zero the meter needle. (This adjustment should be repeated occasionally.) Make sure that the cells and holder are seated properly, then replace the compartment cover and place the solvent solution, or "blank," in the light path. Turn shutter switch on. Rotate slit knob accurately to zero the needle (see paragraph 6). Operate the slider knob to place an unknown sample in the light beam. Set selector switch to 1.0. Rotate transmittance knob to zero the needle again. Record the transmittance, or density reading - set switch to 0.1 if transmittance is less than 10%. Place the next unknown sample in light path and zero needle by rotating transmittance knob.

Special Directions for Hydrogen Tube Installation

1. Take off the top of the tungsten lamp housing and pull up the locking slide located

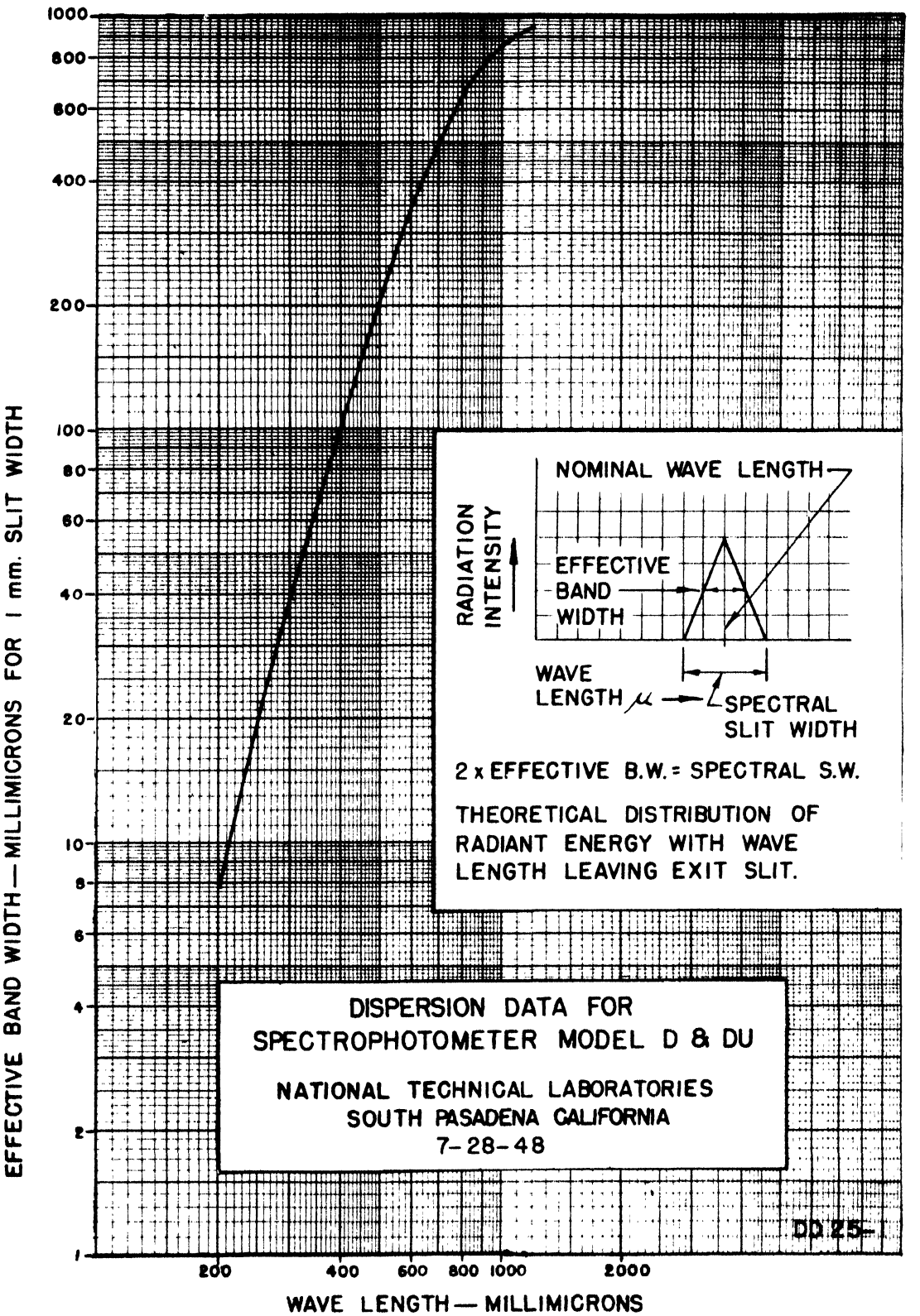


Fig. IV-13. Band width vs. wavelength for Beckman Model DU Quartz Spectrophotometer (Courtesy of National Technical Laboratories)

next to the monochromator.

2. Remove the tungsten lamp housing from the alignment pins and set it aside.

3. Pull up the locking slide in the hydrogen tube housing, set the housing in position on alignment pins, and lock it in place by pushing down the slide.

Operation

1. Plug the power supply into the 110 volt, A.C. line.

2. Turn the switch to the ON position, and allow 1 minute for warm up of the filament.

3. Press the button located at the right of the switch to start the arc in hydrogen tube. For the first 5 minutes, while regulating tubes are warming up, the current through the arc will gradually increase to its final regulated value, after which the light output of the lamp will remain constant.

Occasionally, the discharge may be limited to the inside of the anode compartment of the tube. This condition is encountered most often when the tube is hot from previous operation at the time the power supply is turned on. In case this happens, the power should be turned off immediately, the lamp allowed to cool, and then the starting procedure repeated.

Operating Instructions for Coleman Model 10S Double Monochromator Spectrophotometer[10]

General Instructions. Attached to the spectrophotometer are a red and black rubber covered twisted pair, a service cord and plug, and black, red, and white terminals corresponding to terminals on the intensity meter (Coleman pH meter). Connect the red lead of the twisted pair to the positive terminal of an 8 or 10 volt storage battery, and the black lead to the negative terminal. Connect the corresponding terminals of the spectrophotometer and the intensity meter, using leads of color similar to the terminals and keeping the white lead away from the other leads. The service cord is now connected to any 110 volt, 60 cycle current outlet, and the spectrophotometer is ready for use.

When the spectrophotometer is turned off and the service plug is connected, the battery is charged by a trickle charger built into the spectrophotometer. If the spectrophotometer is not to be used for some time, the service plug should be disconnected to prevent overcharging of the battery.

10. Adapted, by permission, from the operating instructions furnished by the Coleman Instrument Company,

Changing Slits. This operation is delicate and should be done by someone with experience. Before changing slits for the first time the operator should study the diagram of the working parts of the spectrophotometer.

Four exit slits are furnished with the spectrophotometer. These pass light beams, 5, 7.5, 15, and 30 mμ wide. For samples with sharp absorption bands, a narrow slit should be used, whereas a broader slit is permissible if the absorption bands are not sharp. All the slits are adjusted so that the wavelength dial indicates the wavelength passing through the center of the slit.

To change slits, remove the cuvette carrier and disconnect all leads except those to the battery. Set the wavelength dial at 350 mμ, then stand the instrument on its back with the panel away from the operator. Open the small door on the right-hand side. The slit is at the top of this chamber and is held in by a set screw at the end of a hole about an inch long. On loosening the screw, the slit will fall out. Now turn the spectrophotometer on its front edge and put in the desired slit with the brass slit faces up and the number on the holder at the right. Turn the "On-Off" switch to ON. By inserting the index finger in the right-hand hole in the bottom of the instrument case the levers holding the diffraction gratings may be moved upward against the pull of a string. (If the levers are allowed to snap back the instrument should be recalibrated.) When this is done an image of the first slit may be registered over the exit slit. Turn the exit slit so that it is exactly parallel to the projected image, tighten the set screw, and again check the alignment. The levers should now be allowed to move back slowly until they come in contact with the cam attached to the wavelength dial.

Measuring Per Cent Transmittance

a. Introduction. For the preparation of absorption spectrum curves, the amount of light transmitted by a solution must be compared with the amount of light transmitted by the solvent under similar conditions.

Round and square cuvettes are supplied for the solutions. The round cuvettes may be used for preparation of qualitative curves; the square cuvettes allow the calculation of exact extinction coefficient values. Cuvettes are supplied in matched pairs, with etched serial numbers and lettered A and B. The round cuvettes are placed in the cuvette holder so that the index line marked at the top points to the rear of the instrument. The square cuvettes are placed with the letters A and B in back.

b. Steps in Measuring per cent Transmittance of Solutions

1. Place the cuvette carrier in its housing so that the small raised cone is at the right. Fill cuvette A half full of the solvent; place it in the left-hand chamber of the cuvette carrier; then fill cuvette B half full of the solution and place cuvette B in the right chamber. (After filling the cuvettes it is advisable to wipe them with Kleenex or a soft towel. After use, clean the cuvettes carefully, both inside and outside. Swabs on wooden sticks may be used.)

2. Check to see whether the instrument is properly set up.

3. Turn the "Hi-Lo" switch to LO. This markedly increases the life of the lamp. It may be necessary to use the lamp on HI when using small slits, and near the extremities of the spectral range of the instrument.

Turn the "On-Off" switch of the spectrophotometer to ON and allow about 5 minutes for the battery and rectifier to become stabilized. Set the four knobs of the decade resistance to zero. Now turn on the intensity meter by lifting button "B." Turn the "Scale Switch," marked 1-10, clockwise.

4. Place the cuvette holder in mid-position to intercept light from the exit slit and darken the photocell.

5. Set the intensity meter scale at exactly zero, using the mirror scale to avoid parallax. Adjust the "AP" knob of the intensity meter until the milliammeter needle remains at rest when button "P" is pushed down. (Only the initial swing of the needle is significant; disregard any movement when the button is released.)

6. Set the "1000" knob of the decade resistance in the spectrophotometer at the 10 position, and turn the "B" knob of the spectrophotometer until the intensity meter is brought to a balance, as above.

7. Push the cuvette carrier to the extreme right, thus placing the solvent in the light path.

8. Adjust the dial of the intensity meter (Coleman pH meter) to read exactly 100 or pH 10.

9. Adjust the wavelength dial to the desired value, using the mirror scale to avoid parallax. Now adjust the spectrophotometer decade until the intensity meter is balanced. The knob marked "VER," on the intensity meter, may be used to complete this adjustment if desired. (If the intensity meter deflects to the right when button "P" is depressed, add more resistance. If balance cannot be obtained with the full decade, move the "Hi-Lo" switch to HI. If balance still cannot be obtained, turn the "scale switch" counterclockwise. Each division on the potentiometer dial now corresponds to 6 millivolts rather than 60, and the accuracy with which the potentiometer dial may be balanced is reduced.)

10. Move the cuvette holder to the extreme left, thus placing the solution in the light path. Without disturbing other settings adjust the intensity meter potentiometer dial until the instrument is balanced. Read the per cent transmittance directly from the potentiometer dial.

11. Move the cuvette holder to the extreme right and balance the intensity meter by turning the potentiometer dial. It should read very close to 100.

12. Repeat steps 8 to 11 inclusive at each desired wave length. The readings of the wavelength and intensity meter dials should be recorded.

13. Occasionally check the dark current setting (steps,4, 5, and 6). The "zero setting," which produces coincidence of the spectrophotometer and intensity meter at zero potential, should be checked about every fifth reading. To do this the decade resistance and the potentiometer dials are brought to zero, and balance is obtained by adjusting the "AP" knob.

Notes:

1. If a high potential is applied to the intensity meter it may become "blocked" or insensitive while the accumulated charge slowly leaks away. To unblock the intensity meter, first turn the meter off by depressing button "B." Disconnect the lead from the red jack. A wire for unblocking the meter is provided. One end of this is fitted into the red jack; the other is pushed down through the small hole in the instrument panel beside the milliammeter until it touches the grid post. This unblocks the electrometer, which may now be reconnected.

2. The relative error in reading per cent transmittance increases as either very high or very low values are obtained. The optimum transmittance range is from 10% to 60%. Several solutions of varying concentrations should be made up, so that as many measurements as possible may be made within the optimum transmittance range by choosing suitable concentrations.

Operating Instructions for Cenco-Sheard Spectrophotelometer[11]

1. The side of the "Spectrophotelometer" should be substantially perpendicular to the optical bench and the entrance slit should be

11. Adapted from the instructions furnished by the Central Scientific Company.

in the optic axis of the bench. Plug both power plugs into a 110 volt, A.C. line. One plug lights the large lamp and the other lights the galvanometer lamp. The proper orientation of the instrument is determined by observing when the maximum amount of light falls on the grating. To do this, remove the knurled screws at the back of the instrument and, with an entrance slit of 1 mm. or more, study the illumination of the grating when the instrument is adjusted with reference to the bench. It may be necessary for the observer to check this position again to determine whether the instrument is properly aligned for various positions of the light sources and other bench accessories.

2. To locate the light source properly with reference to the entrance slit, adjust the instrument until the wavelength indicator shows a wavelength of 400 mμ. Note: The first dial always reads zero. Do not turn the counter beyond the limits 0250 to 0850.

Set the entrance and exit slits at 1 mm. and 5 mμ, respectively. (The openings in the exit slit are, respectively, 5 mμ, 10 mμ, and 20 mμ. The small slit with only one opening is 2.5 mμ.)

Move the light back and forth until the galvanometer shows maximum deflection. It will be observed that this occurs when the image of the filament, about 5 mm. wide, is well defined on the entrance slit. It will be observed also that more useful light is available when the width of the image of the filament is neither too broad nor too narrow. The distance from the center of the lamp bulb to the "Spectrophotelometer" for this optimum condition is about 36 cm.

Use no absorption cell for these adjustments and push the carriage completely to the left. Cover the round hole in the top with the round plug provided for the purpose.

3. Select such values of the entrance and exit slits as will fulfill the following conditions:

a. The reference reading on the solvent should be as large as possible - 80 to 100.

b. Use as narrow a slit as possible, especially the exit slit, particularly when working with substances possessing narrow absorption bands.

4. Adjust galvanometer to zero using the lever on the galvanometer case. Fine adjustments are made by sliding the frosted glass window to the right or left.

5. Adjust wavelength to desired value by turning crank. Always approach the final setting in a clockwise direction, that is from lower wavelengths to higher wavelengths. If the indicator should be turned beyond the point desired, the crank should be reversed four or five turns and the setting made precisely while the crank is turned in a clockwise direction.

6. Place the solvent in the left compartment of the holder and the solution in the right compartment.

7. Place the solvent in the light beam (be sure the viewing tube is up) and note the galvanometer deflection, I_0.

8. Immediately move the solution to be measured into the light beam and note the galvanometer deflection, I. The ratio I/I_0 is the transmittance value of the solution for the particular wavelength shown by the indicator.

9. For measurements below 410 mμ use the blue filter in the filter holder just before the entrance slit. For measurements above 650 mμ use the red filter. Otherwise, no filter is needed to eliminate stray light.

Note: If high precision is not required, pyrex test tubes may be used as sample containers. They are placed in the hole in the front of the instrument and covered with the black metal tube to eliminate stray light. Center the hole in the carrier below the hole in the instrument casing and place the forked metal piece, forks downward, astride the bottom of the slide to the left and against the side of the regular cell support. When the slide is clicked into position for the use of tubes, the plate is held in proper position to prevent stray light from entering the tubular cell compartment from the right side of the carriage.

Determination of the Absorption Curve of a Substance. A substance will be assigned to each student by the instructor. The range of wavelength to be investigated and the instrument to be used will also be designated. No general rule can be stated concerning the strength of solution to be prepared. Usually a 0.01 to 0.001 M solution is sufficiently concentrated for the lowest optical densities and other concentrations are prepared by dilution. A concentration should always be selected such that the optical density will lie between about 0.3 and 1.5.

Plot molar extinction coefficient as ordinate vs. wavelength in millimicrons as abscissa.

Determination of the Concentration of a Substance. Select the wavelength of maximum absorption for the compound and construct a calibration curve by measuring the optical densities of four or five concentrations of the substance at this selected wavelength. Plot optical density vs. concentration. If the substance obeys Beer's law a linear calibration curve is obtained. Measure the optical density of the unknown substance and obtain its concentration from the calibration curve.

If it is known that the substance obeys Beer's law, the molecular extinction coefficient can be calculated from one measurement on a standard solution and the unknown concentration is then calculated using this coefficient and the measured value of the optical density.

To determine vitamin A in fish oils, weigh 1 g. of the oil into a 100 ml. volumetric flask and dilute with isopropyl alcohol to 100 ml. Measure the extinction of this solution in a 1 cm. cell at 328 mμ. The potency of the original oil in International Units is

$$\text{I.U. per gram} = E^{1\%}_{1\text{ cm.}} \times 2200$$

Spectrophotometric Determination of pK Values of Indicators and Other Substances.

If the optical densities of a series of solutions of an acidic or basic substance in different buffered mixtures are plotted against the pH, the pK of the substance can be determined. The pK is equal to the pH at the point where the optical density is halfway between the minimum and maximum values. The concentration of the substance must be kept constant in all solutions. The most sensitive measurements can be made if the wavelength chosen for the measurement is that of minimum transmittancy for one of the forms of the substance. Either pKa or pKb may be determined in this manner.[12]

Apparatus and Reagents. Suitable spectrophotometer and absorption cuvettes.

0.05% stock solutions of various sulfonephthalein dyes. (See page 150 for directions for their preparation.)

Standard stock solutions for preparation of buffers.

Procedure. Prepare 20 ml. each of a series of nine to twelve buffer solutions according to the directions of Table 1, page 136-137, having pH values separated by 0.2 to 0.4 pH units and extending over the entire range of the indicator. Measure out 5.0 ml. of the proper stock solution and the proper amount of acid or alkali accurately with a buret or pipet into a graduated cylinder. To each buffer solution add the same amount of 0.05% indicator solution (an amount which, by trial, will give about 10% transmittancy when the indicator is fully transformed into the form with the predominate color (red, blue, or purple)), then dilute the solution to 20 ml. with distilled water.

Rinse out the absorption cuvette with the solution to be used, and then fill the cuvette. Distilled water may be used as the comparison solution. Measure the complete absorption curve for at least one solution whose pH lies in the middle of the indicator's range. The transmittancy of the remainder of the solutions may be determined at the wavelength of minimum transmittancy which was found from the complete absorption curve. (See also page 141.)

Plot the log transmittancy, or optical density, for each buffer solution, which was found at the wavelength of minimum transmittancy, against the pH of that particular buffer solution. A curve similar to Fig. IV-14 will be obtained. The pH at the point where

$$E = \frac{E_{max.} + E_{min.}}{2}$$

is equal to the pK of the indicator.

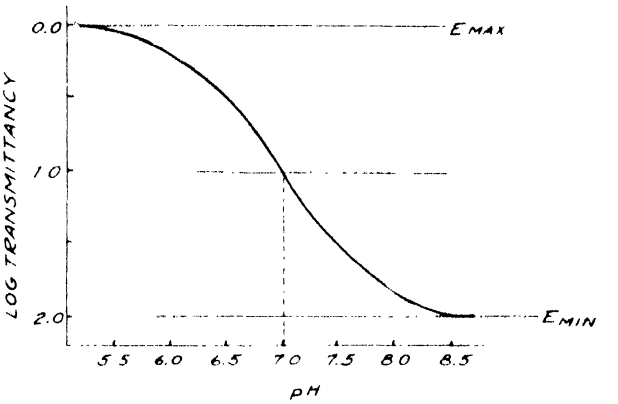


Fig. IV-14. Relation of pH to per cent transformation of bromthymol blue (pK = 7.0).

Operating Instructions for Beckman Model IR-2 Infrared Spectrophotometer

Note: It is impossible to include here a complete set of operating instructions for such a complicated device as the automatically recording infrared spectrophotometer. Only a bare outline of the essential operations necessary in the measurement of liquid samples will be included. It is assumed that the instrument has already been properly installed. The reader is referred to the complete instruction book furnished by the makers.

1. Warning. Lethal voltages appear at several points in the amplifier circuits in normal operation and may appear almost anywhere in the wiring, including the control panel circuits, if a fault has developed.

12. Brode, W. R., J. Am. Chem. Soc., 46, 581 (1924). Stenstrom, W. and Goldsmith, N., J. Phys. Chem. 30, 1683 (1926), Phillips, J. P. and Merritt, L. L., J. Am. Chem. Soc. 70, 410 (1948).

Never touch the amplifier wiring without first turning the POWER switch OFF.

Never turn amplifier POWER switch to ON with control panel (10 cycle amplifier) plug removed or with any tube out of its socket.

2. Constant Temperature Bath. The thermostat has been adjusted to 25°C. Be sure that the oil level in the bath is such that the tip of the red metal rod is between the two black lines on the level indicator rod inside the transparent lucite cover. Turn the line switch to ON. The heater switch should be on the LOW position. Cooling tap water should flow through the cooling coil of the bath since, in normal operation, heat will have to be removed from the spectrophotometer.

3. Power. Check amplifier D.C. milliammeter zero adjustment, tapping it with pencil or fingernail, and readjust if necessary. Turn GLOWER switch OFF, OUTPUT switch to LINEAR, and POWER switch ON. The D.C. meter monitors the regulated power supply for the entire amplifier unit. The meter should rise to 150 to 180 milliamperes, then should stand there for about a minute while the regulator tube filaments warm up. Depress the STARTER switch and hold until meter rises to 200 milliamperes and completely stops drifting. If this is not exactly at the 200 mark alter the setting of the POWER ADJUSTMENT control to bring it to the correct value keeping the STARTER switch depressed meanwhile.

Electric heaters are installed in the amplifier to prevent damage to insulation from humid atmospheres during nonoperative periods. They are turned on by the POWER switch in the OFF position.

Note: To avoid the slight drift of light output and zero which occurs when the amplifier is warming up, leave amplifier and glower turned ON except for inactive periods of more than 5 minutes. For most convenient operation, turn on 30 minutes before use.

4. Glower and Heater. Turn the METER switch to GLOWER and the GLOWER switch to ON. This puts current through the starting heater for the Nernst glower light source. Within 2 minutes the amplifier A.C. ammeter should indicate that the glower is passing current. If the current rises considerably above normal, the 1 ampere GLOWER fuse at the rear of the amplifier may burn out. If this occurs, turn the light gate counterclockwise with a screwdriver until it is flush with the wall top. The light gate is recessed in the wall between the lamp and the phototube and the screw is made accessible by removing the half-inch hole plug in the top of the lamp house. Replace the fuse and try again. When the meter indicates that the glower is conducting, adjust the glower current to 0.8 ampere by turning the light gate clockwise; then check the glower regulator current by turning the meter switch to REGULATOR. The needle should stand between 0.60 and 0.69 amperes for normal line voltage. If it does not, the current can be increased or decreased by about 0.08 amperes by throwing the REGULATOR switch to HIGH or LOW, respectively. Use whichever position brings the current nearer to 0.16 ampere less in the REGULATOR than in the GLOWER position of the METER switch.

If the glower fails to start, turn the GLOWER switch to OFF, remove the cover of the lamp compartment, and made sure that the heater filament comes to a moderate red heat when the GLOWER switch is turned ON. If it does not, make sure the glower assembly is properly plugged in and that the heater leads are securely attached to their binding posts (see section VI, Maintenance, of the bulletin furnished by the manufacturer), and that the heater and glower are intact. If the glower still fails to start, inspect first the 1 ampere fuse at the rear, then the 1.0 ampere fuse under the left-hand cover plate of the amplifier, mounted on the vertical divider (or check to determine that 115 volts A.C. appears across the glower pins in the glower assembly). If both fuses are intact, replace the glower.

The heater winding is tapped at 13, 15, and 17 volts to permit adjustment for varying heater resistance. The heater tap is normally set on the 15 volt terminal, which will result usually in a satisfactory compromise between prompt glower starting and long heater life. An equally important factor in achieving prompt starting is adjustment of spacing between glower and heater to a minimum by rotating the glower in its holder.

5. Damping Control. Turn OUTPUT switch to NULL, PERIOD control switch to 2 seconds, potentiometer control to ZERO, GAIN switch to 1, and GAIN control to maximum (counterclockwise limit). Move the shutter slide to "MTL" and adjust the ZERO control on the amplifier to center the needle of the null meter on the control panel.

Set the wavelength control at about 6 μ, the slit control at 0.1 mm., and open the metal shutter momentarily. The null meter will go off scale to the left, indicating that the instrument responds to light. A few seconds after closing the shutter again it will come back on scale. The manner in which it returns to zero, whether under- or over-damped, can be regulated by the damping control. A desirable adjustment permits the needle to over-shoot one or two divisions. The adjustment is not critical and does not affect the eventual reading.

6. Period Control. The output of the amplifier goes through a filter. The time constants of the filter can be varied to give a period of 2, 8, or 32 seconds. The slow response decreases the random fluctuations of the output, or the "noise," by two-fold for each step by removing the higher frequency components.

Where the decreased response rate can be tolerated, the lessened "noise" permits operation at high amplification and with narrower slits, and so assists the indicator system to further exploit the optical resolving power of the monochromator.

The sensitivity varies slightly with the PERIOD control setting. Consequently, both the CHECK, or 100%, and the transmitted light settings must be made at the same position of the PERIOD control.

To obtain a rapid reliable reading at the longest period, attempt to continuously zero the meter needle while holding the PERIOD control for 2 seconds in the first or 2-second position, then 8 seconds in the middle, and finally for 32 seconds in the last position.

7. Output Terminals. Terminals are provided on the amplifier control panel for operation of a commercial potentiometer-recorder or other indicating device requiring not over 1 milliampere at 1 volt or less for its operation. For proper indication, the switch above them should be turned to the LINEAR position. A 50 ohm resistor, mounted directly behind the "+" terminal, is standard equipment for operating a recorder of 50 millivolt scale span such as the Brown Recorder furnished with the instrument. (For other recorder ranges it should be replaced by a wire-wound resistor of resistance in ohms numerically equal to the recorder full-scale millivolts. For operating a 1 milliampere meter, the resistor should be disconnected. In this case the "+" and "-" terminals must be shorted together when the meter is disconnected.)

In general, each indicating device used will require a different setting of the DAMPING control for optimum results.

The "M" terminal provides a marker circuit to indicate wavelength positions or other information on the recorder chart. Shorting it to the "-" terminal, as by a key, will cause the recorder pen to deflect 2 millivolts toward 100% while the key is depressed.

A marker switch is incorporated in the IR216 Synchronous Motor Wavelength Drive, which when properly adjusted and connected across the "M" and "-" terminals can be used to mark the recorder chart. The Wavelength Drive is arranged to insert a mark at each of the red lines superimposed at 30 degree intervals on the wavelength scale.

8. Density or Transmittance Measurements. Absorption cells are provided in pairs in the Model IR-2 Spectrophotometer to facilitate setting the sensitivity to 100% without having to remove the sample from the cell at each wavelength.

It is necessary to make a preliminary comparison of the transmittance of the empty or solvent-filled cells, preferably relative to the blank path because this gives initial information about the condition of the cell windows. However, at wavelengths where CO_2 or water vapor in the air absorb appreciably, the blank position cannot be used. Here it is convenient to use an empty or solvent-filled cell to set the check adjustment

Use the null potentiometer for the comparison. Set the wavelength and slit controls to a value to be used. Check the zero with the metal shutter, then, using the glass or metal rotating shutter depending on the wavelength, set the gain controls to balance at check for the blank cell position. Insert first one cell, then the other, balancing for each with the potentiometer on the READ switch position and recording the density or transmittance value for each. For highest accuracy, these readings should be rechecked after each use of the cell to insure that the sample did not contain substances which altered the transmittance of the cell windows.

After filling an absorption cell with sample, repeat the above adjustments and readings. The optical density of the sample is taken as the difference between the sample reading and the standardization reading for the same cell. The sample transmittance is the ratio of the transmittance readings for sample and cell.

9. Filters and Shutters. Two rotating shutters are provided - a metal one for use from the short wavelength region to 9 μ, and a thin glass one beyond 9 μ. The latter serves to correct for the "first order false energy," or scattered light of shorter wavelengths, because it does not interrupt it. The scattered light is consequently included in the background radiation "seen" by the receiver and ignored by the frequency selective amplifier.

The rotating glass shutter serves the same function as the lithium fluoride shutter in conventional, continuously illuminated thermocouple instruments, with the added convenience that the zero point is unaltered by its use.

The metal shutter slide carries two blank positions, in one of which a magnesium oxide or lithium fluoride filter may be installed if desired. Use of the lithium fluoride filter as a shutter, with the inconvenience of altering the zero setting at each wavelength, is not recommended.

The magnesium oxide filter reflects radiation over a broad band below 2 μ and con-

sequently is useful to limit scattered light at longer wavelengths.

10. Band Identification and Turret Settings. The wavelength scale calibration in the Model IR-2 Spectrophotometer is reliable to 0.1 μ. It is a convenient aid to location of absorption peaks, using published curves of absorption in the region of interest as a guide.

With a standard sample in the absorption cell, and slits set to the value to be used in the analysis, open the metal shutter and decrease the gain until the null potentiometer balances at about 5% transmittance.

Search for the absorption band peak, using the null meter as an indicating device and decreasing the gain if necessary to keep deflections within the limits of the needle deflection range. When the absorption peak is found, increase the GAIN control to locate it accurately, turning the potentiometer to balance out most of the increased deflection. For most reproducible wavelength dial settings, approach the final value from the long wavelength side. This is the direction which stretches the loading spring holding the cam follower against the wavelength drive spiral cam.

To set a turret pin to this wavelength, select a turret pin of length appropriate to the wavelength region in question from Table 5.

TABLE 5. TABLE OF TURRET PIN SETTINGS

Pin No.	Approx. Pin Setting in Microns	Approx. Range in Microns
1,2	0.8	end. -2.5
3,4	2.5	0.8 -6.0
5,6	6.0	2.5 -8.5
7,8	8.5	6.0 -10.0
9,10	10.0	8.5 -11.5
11,12	11.5	10.0 -13.0
13,14	13.0	11.5 -14.3
15,16,17	14.3	13.0 -end.

Turn the turret release control counterclockwise to OUT and the pin selector to the desired pin position. GENTLY return the release control to IN. Remove the small hole plug to the left of the turret. Release knob and with a small screwdriver (approximately 3/32 inch blade) loosen the set-screw clamping turret pin. Remove the small hole plug in front of the pin, just above the pin selector. With a screwdriver having a blade 1/4 inch wide, turn the pin IN (clockwise) until the null meter just starts to move, indicating that the turret pin has come into contact with the wavelength arm. Turn the wavelength dial out of the way. Carefully and very slowly scan across the absorption peak by turning the turret pin, noting the point of maximum deflection of the null meter needle, which should be set on the graduated scale. Turn the turret pin very slowly, counterclockwise until this deflection is again reached. Lift the wavelength arm with the release control and gently return it to the pin. If the deflection is less, turn the pin slightly clockwise and try again, until the maximum deflection is again reached. Clamp turret pin. Replace the hole plugs, release the wavelength arm, turn the selector to zero and gently reengage the continuous wavelength dial. WARNING: Do not turn the turret pin selector until the release control has been turned to OUT.

11. Automatic Wavelength Drive.

Mounting. If the automatic wavelength drive and the recorder are to be used they will already have been mounted by the instructor. See the instruction book furnished by the manufacturer for details.

Operation. Disengage the clutch by turning clutch handle to a vertical position. Turn wavelength dial to desired position, start the motor and engage clutch by turning the handle to a horizontal position. The switch positions are as follows:

FWD. - Wavelength dial turns from long to short wavelengths.
OFF
REV. - Wavelength dial turns from short to long wavelengths.

Shifting Gears. The gear shifting mechanism used in this attachment is slightly difficult to shift when the motor is not running, or is running opposite to the direction of rotation of the drive gears. It is therefore recommended that the gears be shifted from high to low speed with the motor switch in the REV. position and from low to high speed with switch on FWD. Depress the detent release knob, turn the gear shift lever in the desired direction until the index is almost to the new position and release the detent knob. It may require some "hunting" with the shift lever before the detent pin will engage.

Marker. The marker switch is actuated by a two-position cam mounted on the idler gear and can be used, if desired, to "mark" the recorder record at each 30 degree rotation of the wavelength dial. When the marker switch is closed, the recorder pen will be deflected approximately two divisions (1 millivolt) and will remain in that position until the marker switch opens. It is difficult to adjust the marker switch so that only a "pip" will appear on the record, particularly

at slow speeds; therefore it is desirable to allow the switch to operate normally and refer to the leading edge of the "mark" as the reference position. The marker switch terminals are connected to a "tiepoint" located at the back of the wavelength drive. These may be connected with a pair of wires to the "M" and "-" terminals on the amplifier.

Speeds. The standard wavelength drive is equipped with motor and gear combinations which will traverse the entire wavelength range (4 revolutions of the dial on 60 cycles) in approximately 12 minutes, 18 minutes, and 43 minutes.

12. Automatic Recording of Spectra. It is recommended that the instrument be set by the manual method to read about 100% transmittance for the solvent or blank cell at the shortest wavelength (down to about 3 μ) of the record to be made. A run over a range of 2 to 3 μ is usually all that can be well recorded. Turn the wavelength scale back to the longest wavelength of the run to be made. Turn the switch above the output terminals to LINEAR. Turn on the chart drive switch just inside the glass panel of the recorder. (The instrument power switch is left ON all of the time except when servicing the instrument or during shutdown periods of longer than one week. If the recorder has been turned off, swing the chassis out of the case and turn ON the instrument power switch located on the rear of the chassis. Allow a few minutes for the tubes to warm up.) Standardize the battery current by depressing and releasing the push button on the front of the chassis. If the indicating pointer drives toward either end of the scale, wait a few seconds and then depress the push button again. Repeat this procedure until the pointer does not move. If the pointer persists in moving to the upscale limit, a new battery must be installed.

If the chart is inking properly, the automatic recording can be started by starting the automatic wavelength drive motor. Be sure to stop the wavelength drive motor at the end of the run desired. Turn the chart drive motor OFF. Repeat the run over the same wavelength range with the solution cell in the beam.

13. Shutting Instrument Off. When the necessary readings or recordings are completed, turn the GLOWER switch to OFF and the POWER switch OFF. Turn the chart drive motor of the recorder to OFF, if the chart drive is still running. Turn the OUTPUT switch to LINEAR and the METER switch to GLOWER and the PERIOD switch to 2, so as to be ready for the next operator.

14. Filling Liquid Absorption Cells. Loosen bottom valve approximately one-half turn. Hold cell in cleansing tissue with cell inverted so that bottom of cell is at an appreciable angle above the horizontal. Remove needle from filled hypodermic syringe, remove knurled needle fitting from upper valve, and insert tip of syringe in this valve body. Force clean solvent through cell. When cell is completely clean it may be desirable to evaporate the solvent by forcing dry air or nitrogen through the cell from an empty syringe. Repeat this procedure with solution, filling the cell until a little overflows on cleansing tissues held at the valve on the opposite end of the cell.

Hold cell level and tighten bottom needle valve using caution so as not to injure the valve. A 1/4 inch screwdrive-handle socket wrench is recommended.

Hold cell upright, insert hypodermic needle into stem and withdraw excess liquid to approximately 1/4 inch below valve seat. This forms an air pocket which helps to prevent the liquid from being forced out at the seals if the temperature of the liquid rises when the cell is inserted into the light beam. In some instances where materials must be handled under anaerobic conditions the size of the air pocket may be considerably reduced or the valve replaced by a solvent resistant stopper which can be perforated by a hypodermic needle to introduce the sample.

Hold cell upright, insert, and tighten top needle valve. Inspect cell for presence of air bubbles in light path.

Determination of Infrared Absorption Spectrum of a Solution.

The instructor will assign a substance and indicate the solvent to be used. Measure the absorption spectra over the range either by the manual or automatic recording method as indicated by the instructor. If the measurements are done by the manual method, plot per cent transmittancy or, better, the optical density versus wavelength in microns. If the measurements are automatically recorded, calculations will have to be made at several wavelengths from the data on the chart to obtain the necessary points to plot. The automatic record is more useful to indicate the approximate appearance of the spectrum and to locate suitable bands for quantitative measurements and less useful for calculations of the absorption spectrum. The band width at any slit setting and for any wavelength can be calculated from the dispersion data in Fig. IV-15.

Determination of Concentration

Several methods for the calculation of con-

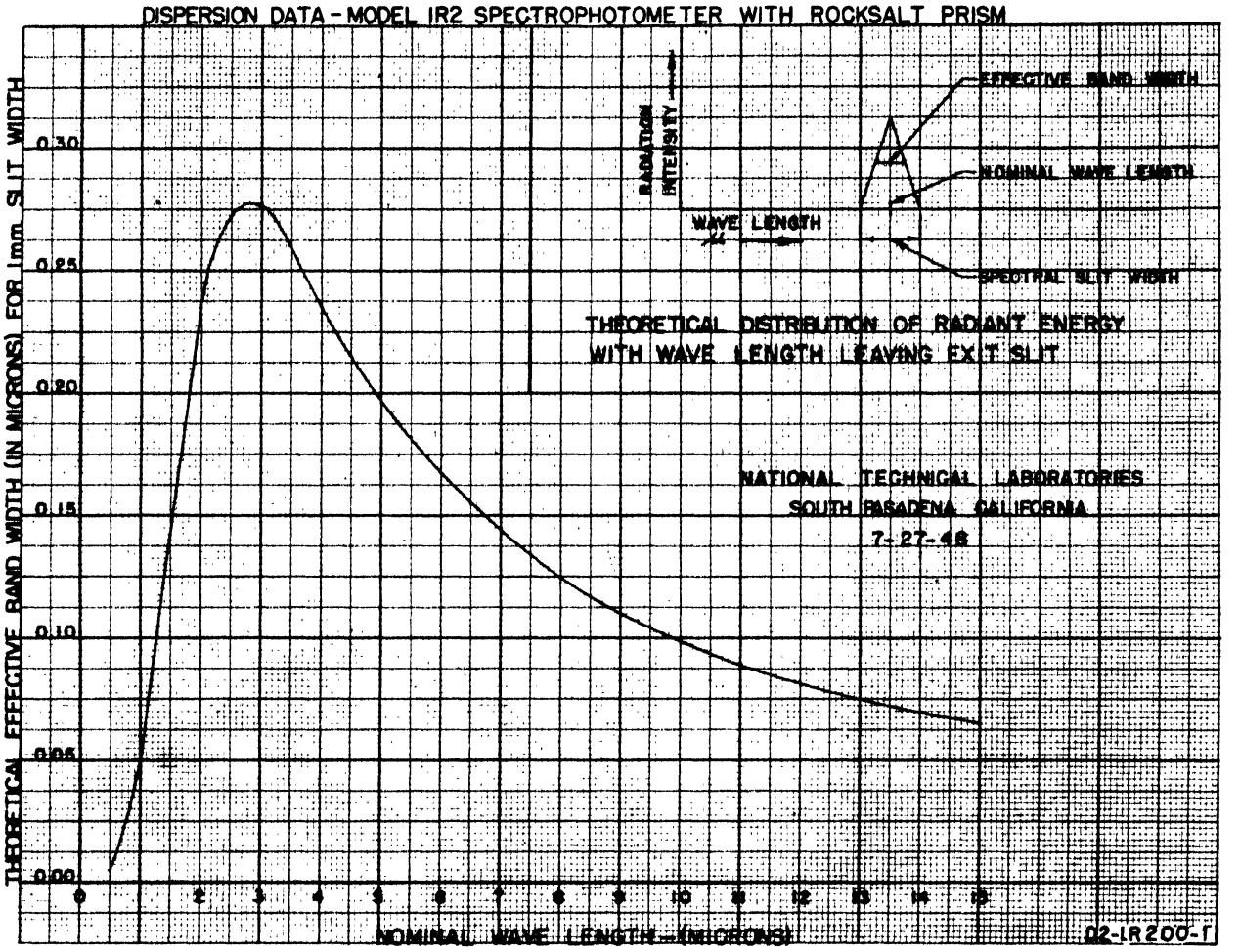


Fig. IV-15. Dispersion data for Beckman Model IR2 Infrared Spectrophotometer with rocksalt prism (Courtesy of National Technical Laboratories)

centration from infrared data are possible. In one method a series of standard solutions are prepared and the optical density of each solution is determined at a selected wavelength. Unknowns are then compared to the working curve so prepared. Select the most suitable wavelength from a consideration of the absorption spectrum curve if that has been previously measured. Set a turret pin to this wavelength (see directions for instrument, above). Measure manually the optical density of the standard solutions and then that of the unknown. Use the same cell for all of the solutions and reserve the second cell for the solvent. Plot optical density as ordinate against concentration as abscissa.

LABORATORY WORK WITH THE BECKMAN FLAME PHOTOMETER

Operating Instructions

1. Before beginning a determination, several preliminary steps must be taken to convert the Beckman spectrophotometer for use as a flame photometer. These will have been taken care of before work is begun, but they are included for completeness.

a. The 2000 megohm phototube load resistor in the phototube housing must be replaced by a 10,000 megohm resistor. The latter should not be handled with the bare fingers as its resistance is changed by a film of

moisture or grease. This higher resistance not only increases the sensitivity of the measuring circuit, but also decreases the response time of the amplifier, tending to smooth out the effects of spray and flame variation.

b. The tungsten lamp housing is removed and placed on the burner base assembly. The light from the burner now enters through the opening through which the light from the tungsten lamp formerly entered the monochromator.

c. An aluminum shield is placed over the back of the phototube compartment to protect it from the heat of the flame.

d. The absorption cells and cell carriage are removed completely from the instrument.

e. The spray chamber is clamped into place on the burner base assembly, and the atomizer fitted into place in the ground glass joint of the chamber.

2. The rubber tube serving as a water inlet to the cooling coils of the burner and chimney is connected to a cold water tap. TURN ON THE WATER before lighting the burner to prevent the heat of the flame melting the solder in the burner base and on the chimney coils. The rate of flow is adjusted so that the discharged water is hot, but not boiling.

3. Lighting the Burner. Be sure the air, gas, and oxygen valves on the instrument panel are closed (screwed all the way into the panel). Open the laboratory gascock, then turn on the gas by means of the gas valve on the panel and light the burner. Backfiring, either now or later when the oxygen is turned on, is noisy but not dangerous. It is merely an indication that the gas pressure is too low. If backfiring occurs, turn off the oxygen, then the gas, and begin again. The manometer on the left of the control panel indicates the gas pressure. After lighting the burner, adjust the gas pressure to about a convenient value, 3-5 cm. manometer liquid, by means of the gas valve on the panel.

Next open the oxygen valve on the panel, the stem valve on the oxygen tank, and the hosecock on the reduction valve. Screw in the diaphragm valve on the oxygen tank gauge until the gauge on the instrument panel indicates an oxygen pressure of about 30 inches of water. The flame should consist of a circle of small, regular cones.

4. To atomize the sample, a source of gas pressure up to 30 pounds per square inch must be available, either from a high pressure air line or an auxiliary oxygen tank. Open the laboratory aircock and turn on the air valve on the instrument panel until the gauge on the instrument panel indicates a pressure of 15 to 20 pounds per square inch. Fine adjustment of the air pressure can be made with the air-regulator diaphragm valve on the instrument panel.

5. Flame Adjustments. Both flame size and richness - that is, oxygen and gas pressure, and air pressure - will have optimum values that generally differ slightly for the different elements to be determined. These conditions may also differ for the different wavelengths of a given element, especially if one line is that of the metal and another is due to its oxide. The best pressures for each case will not change and can be accurately reset.

To find them, turn up the gas to give a fairly vigorous flame, adjust the oxygen for maximum response, and then adjust the air regulator to give the most light. When a good air pressure is selected, readjust the oxygen for maximum reading, and then as a final check turn the gas a little higher or lower and adjust the oxygen once more to see if the new maximum is above the preceding one. Record the optimum values of the gas, air, and oxygen pressure.

A maximum with respect to gas is less important than a maximum with respect to oxygen. An optimal flame should show fairly uniform, steady cones. A rapid flicker, however, does no harm if it is not erratic, and does not reduce the steadiness and reproducibility of the transmission dial reading. Optimal adjustment has the double advantage of reducing fluctuations for luminosity to a minimum and rendering the luminosity insensitive to moderate changes of air or oxygen pressure.

When the luminosity of the element being determined is so small that the flame background represents the greater portion of the reading, a compromise is necessary between optimal conditions for the background and those for the total emission.

6. To place the spectrophotometer in readiness, put into place the proper phototube for the spectral region in which the work is to be conducted. Set the selector switch to the ".1" position, turn the sensitivity knob to its clockwise limit, and with the shutter closed (Off), rotate the dark current knob until the galvanometer needle rests at zero.

Under normal conditions, during a minute's observation, the flame background should show no fluctuations exceeding one galvanometer scale division in either direction. The smaller the cones in the flame, or the stronger the intensity of the flame, the less it will be influenced by transitory fluctuations.

7. Slit Settings. The slit can be used over its entire range, but for most purposes a slit width of perhaps 0.05 to 0.2 mm. will be useful. Criteria of sensitivity, precision, ratio of flame background to total light, and necessary resolving power will determine the best slit width. Many of the flame lines to be measured will be narrow, and the photometric response will vary directly as the slit

width. The response to the continuous background, on the other hand, varies as the square of the slit width.

Consequently, during a determination set the slit width to a value that gives no flame background. Then insert the sample to be measured and determine the transmission reading. Remove the sample, increase the slit width, and redetermine the flame background. Reinsert the sample and again measure its transmittancy. If a greater sensitivity is achieved, repeat the preceding steps until the maximum sensitivity has been achieved. However, except when measuring extremely weak emission lines, the flame background should not exceed 10%, since the ratio of metallic emission to flame background determines the precision obtainable.

8. Flame Background. Set the wavelength selector dial at the wavelength desired for measurement. Turn the slit width adjuster to the optimum value, and set the selector knob to ".1" position. (The same sensitivity would be obtained by using the sensitivity knob at its counterclockwise position and the selector knob at the "1" position.) Now open the shutter and balance the galvanometer by rotating the transmission dial. The transmission reading will be the flame background at the desired wavelength. It should not exceed 10%. The narrower the slit, the greater will be the ratio of metallic emission to flame background, and the greater the precision. Record the flame background and close the shutter switch.

9. Sample Transmittance. Place the small beaker containing the standard solution on the beaker holder under the aspirator tip. As soon as the flame becomes colored by the spray, open the shutter and rotate the transmission dial until the galvanometer needle rests at zero. Replace the standard with the unknown solution or a second standard solution, and repeat the balancing. Successive readings should be taken on standards and unknowns. Record the average of these readings and subtract the flame background reading.

The readings should be taken quickly because, if the sample is allowed to remain on the beaker holder longer than 30 seconds, the spray chamber will become too wet and erratic readings may result. The samples should not be allowed to remain uncovered for any length of time since they may lose alcohol by evaporation and thus alter the composition.

Moisture on the inside of the spray chamber will evaporate between readings on samples if the capillary tip is properly constructed.

10. Cessation of Operations. First turn off the compressed air supply, then turn off the oxygen. Finally turn off the gas supply, first the valve on the control panel and then the laboratory deskcock. Disconnect the water inlet. Turn the spectrophotometer selector switch to the OFF position. Clean the beakers, and remove the spray chamber and rinse with distilled water and acetone.

Preparation of Samples

The aspirator of the older model Beckman flame photometer is designed to be used with solutions containing isopropyl or normal propyl alcohol to the extent of 1 part alcohol to every 5 parts of aqueous solution. This ratio produces a finer spray and so-called "dry spraying:" that is, rapid evaporation of the sample in the spray chamber so that little or no moisture collects on the walls of the spray chamber during a determination. The newer, electrically heated, spray chamber eliminates the necessity of using alcohol with the sample.

Fill the small 5 ml. beakers with the standard and unknown samples and place them under a covered dish. They should be removed only for the minimum time required for a reading and then returned to the shelter. This care will reduce evaporation and prevent contamination from dust.

Laboratory Procedure

1. After the flame has been properly adjusted, determine the flame background for the wavelength region 300 to 1000 mμ. Plot the percentage transmission against wavelength. Use a slit width of 0.2 mm. Balance the galvanometer at each wavelength setting by rotating the transmission dial. The curve shows the regions in which a strong flame emission occurs and is useful in later work to avoid difficulties in the interpretation of unknown spectral lines which may become confused with strong flame emission lines.

2. Adjust the air, gas, and oxygen pressures to their optimum values. Place a beaker filled with an unknown solution on the beaker holder and under the aspirator. Determine the emission spectrum of the solution for the wavelength region 300 to 1000 mμ. The spray chamber may become wet during the operation, but the location of the spectral lines or bands may be determined accurately nevertheless. Plot the per cent transmission, corrected for flame background, against the wavelength.

3. Having determined the exact wavelength at which the desired emission line occurs in the preceding step, set the wavelength dial exactly at this value. Insert successively, the standard and unknown samples under the

aspirator and determine the per cent transmission of each solution to the nearest 0.5%. Correct for flame background on each reading, which should be repeated at least five times and results averaged. Obtain the concentration of the unknown from a calibration curve or by interpolation between two known solutions of approximately the same composition, one of slightly larger concentration, and the other of slightly lower concentration.

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CHAPTER V

SPECTROGRAPHY

The spectrograph as an analytical tool has had a long period of development from the discovery of Bunsen and Kirchhoff that the spectra of flames colored from metallic salts were characteristic of the metals. Modern automatic recording spectrographs are capable of giving the percentage of eleven or more components of a sample directly on dials and in a period of less than a minute. Qualitatively, the spectrograph is capable of detecting 0.001% or even less of most of the metallic ions and of certain of the nonmetals, that is, P, Si, As, C, and B, in a sample of only a few milligrams. Quantitative determination of these elements is also easily accomplished. One spectroscopist is usually capable of analyzing as many different samples of the same type of material as five or more men by routine, wet procedures. An accuracy exceeding 5% of the amount of material present is attained for most elements. Consequently, the spectrograph has largely replaced the older, wet analytical procedures for the routine determinations of lesser components of steels, metallic alloys, etc.

Origin of Spectra

A complete discussion of the origin of emission spectra is beyond the scope of this book. For the present purpose, it is sufficient to understand that there are three kinds of emission spectra: Continuous spectra, band spectra, and line spectra. The continuous spectra are emitted by incandescent solids and are characterized by the absence of any sharply defined lines. The band spectra consist of groups of lines that come closer and closer together as they approach a limit, the head of the band. Band spectra are caused by excited molecules. Line spectra consist of definite, usually widely and apparently irregularly spaced, lines. This type of spectrum is characteristic of atoms or ions which have been excited and are emitting their extra energy in the form of light of these definite wavelengths.

The quantum theory predicts that each atom or ion has definite energy states in which the various electrons can exist. In the normal or ground state, the electrons are generally in the lowest energy states. On addition of sufficient energy by thermal, electrical, or other means, one or more electrons may be removed to a higher energy state farther from the nucleus. These excited electrons tend to return to the ground state and in so doing emit the extra energy as light. Since there are definite energy states and since only certain changes are possible, there are a limited number of wavelengths possible in the emission spectrum. The greater the energy in the excited source, the higher the energy of the excited electron, therefore more lines may appear. However, the wavelengths of the existing lines will not be changed.

The intensity of a spectral line depends mainly on the probability of the required energy "jump" or transition taking place. Reversal occasionally decreases the intensity of some of the stronger lines. Reversal is caused by the reabsorption of energy by the cool, gaseous ions in the outer regions of the source. When high energy sources are used, the atoms may be ionized by the loss of one or more electrons. The spectrum of an ionized ion is quite different from that of the neutral atom.

The constituent parts of the spectrograph, including the energy sources and the registering devices, will be considered in the following pages. A few typical, commercially available instruments are then described. Finally the various procedures used in qualitative and quantitative work are described.

Excitation Methods

The flame, an A.C. arc, a D.C. arc, and the high voltage spark are the common methods of excitation. Each has special advantages and disadvantages and special applications.

The flame of a Meker or Bunsen burner furnishes a rather low energy source and the spectra of only a few metals, primarily the alkali metals and the alkaline-earths, are produced. If an air-acetylene, oxy-acetylene, or oxygen and gas flame is used and the sample is atomized into the air or oxygen stream, as in the method of Lundegardh, as many as 43 elements (Ag, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cs, Cu, Dy, Eu, Fe, Ga, Gd, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, Pb, Pd, Pr, Pt, Rb, Rh, Ru, Sc, Se, Sm, Sn, Sr, Te, Tl; Y, and Zn) can be excited. Since the energy available is still not very high only a few lines are produced, but this may be an advantage instead of a disadvantage.

The D.C. arc, produced by a voltage of from 50 to about 250 volts, is a good source and will excite all of the metals. The lines produced are primarily those due to neutral atoms and are

indicated in tables by the symbol of the atom. (Those due to singly ionized ions are indicated by the symbol followed by I, those due to doubly charged ions are followed by II, etc.) The arc tends to wander and flicker especially when struck between carbon or graphite electrodes. This unsteadiness can be reduced somewhat by including a reactance in the circuit (see Fig. V-1).

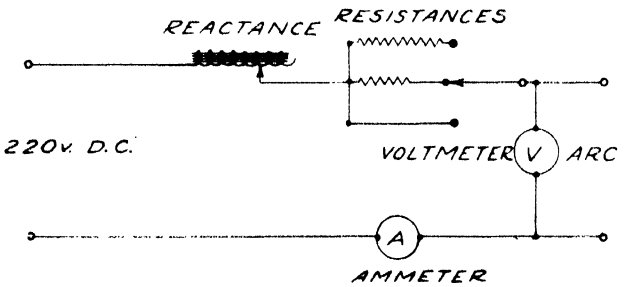


Fig. V-1. Circuit for D.C. arc

The direct current arc is a very sensitive source and is used for the determination and identification of substances present in very small concentrations. A comparatively large amount of the substance being analyzed passes through the arc and, on this account, an average or more representative value of the concentration is shown, whereas the spark may show rather selective results if the material being determined is not evenly distributed throughout the sample. The light from the center portion of an arc is the portion usually employed since there may be local concentration of certain ions near the electrodes. However, since the cathode region gives higher excitation energy it is more sensitive and this region is sometimes employed for the illumination. The electrodes may be composed of the material being investigated if the material is a conductor and will withstand high temperatures. If not, the sample is usually placed in a small core in a carbon or graphite electrode. The upper electrode in such a case is another carbon or graphite electrode ground to a blunt point in a pencil sharpener or a special grinding tool. Many special shapes for electrodes have been devised in order to steady the arc or increase its temperature. For most work, a small crater is ground into the lower electrode. Steadier arcs can be produced if the sample is mixed with pure powdered graphite. Metallic electrodes have some advantages over graphite electrodes but, of course, the lines of the electrode metal will appear in the spectrum. These may serve as a reference spectrum. When carbon or graphite is employed quite intense band spectra due to cyanogen are produced in the violet and near ultraviolet regions and may obscure many desired lines in this region.

Solutions can be evaporated in the craters of the electrodes. If carbon or graphite is employed, the crater is frequently waterproofed by dipping it into redistilled kerosene or collodion.

The lower electrode is usually made the positive electrode. The arc is started by touching the two electrodes together and drawing them apart. If this does not start the arc, a graphite rod may be drawn across the gap.

Graphite is a better conductor than carbon and can be obtained in purer form and is to be preferred in most cases for the electrode material, although carbon gives a somewhat steadier arc. The electrodes can be purified in several ways which cannot be discussed here.[1] The impurities present in Acheson spectrographic graphite electrodes generally will not cause more than a few faint lines to appear in the blanks.

The high-voltage A.C. arc, proposed by Duffendack and Wolfe, employs a voltage of 1000 volts or more. The arc is drawn out to a distance of only 1/2 to 3 mm. or so. For reproducible results, the separation of the electrodes, the potential, and the current must be carefully controlled. The whole assembly must be carefully shielded so as to protect the operator from the dangerously high voltages. The A.C. arc is a steadier and more reproducible source than the direct current arc and otherwise possesses the advantages of the D.C. arc.

The high-voltage spark gives much higher excitation energies than the arc with less heating effect. The spark is produced by connecting a high-voltage transformer (10,000 to 50,000 volts) across the two electrodes. A condenser is usually connected in parallel with the spark gap in order to increase the current. An inductance is also desirable in the circuit since this has been found to decrease the excitation of lines and bands of the air molecules. Large values of inductance decrease the excitation energy and make the spark more arc-like in its characteristics. The relationship between the current, I; potential, E; capacitance, C; and the inductance, L, when a spark first jumps is given by the equation:

$$I = E\sqrt{\frac{C}{L}} \qquad (1)$$

1. See Gibb, T. R. P. "Optical Methods of Chemical Analysis," McGraw-Hill Book Co., Inc., New York, 1942, p. 10.

Thus the characteristics of the spark depend on the capacitance and inductance. Rather elaborate devices are available for allowing variations in these values (see Fig. V-2).

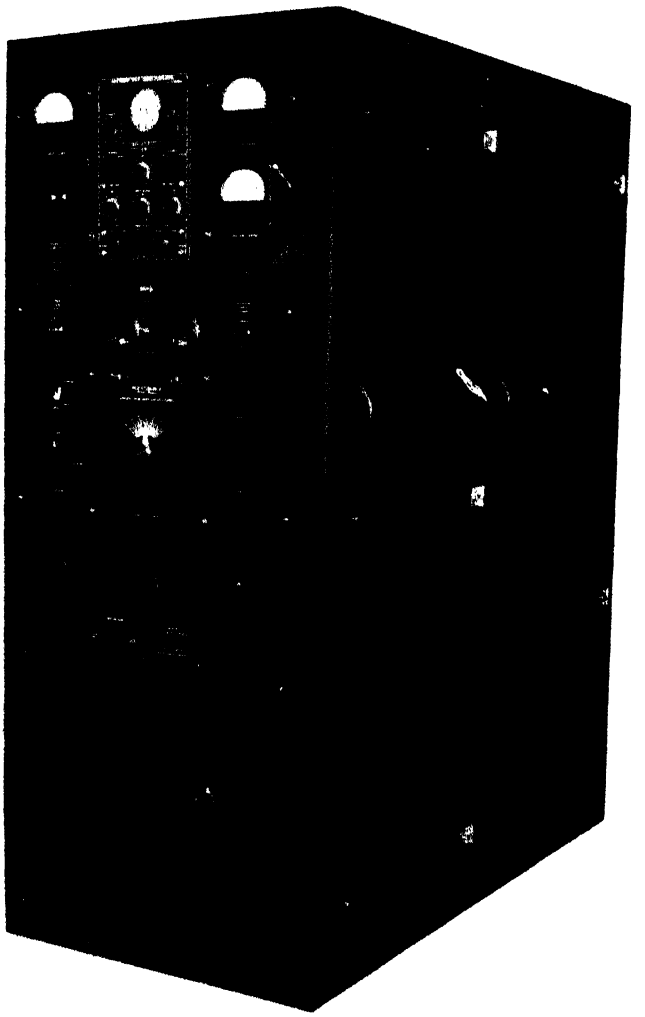
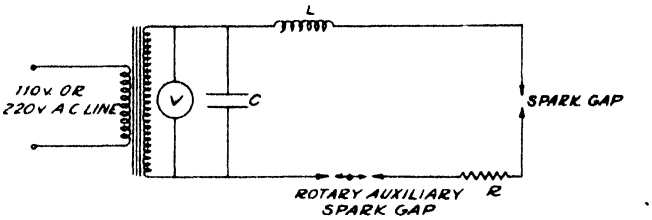


Fig. V-2. Applied Research Laboratories' Multisourse Unit (Courtesy of Applied Research Laboratories)

The circuit proposed by Feussner,[2] Fig. V-3, employs an auxiliary rotating spark gap which is driven by a synchronous motor. The gap is closed for only a brief instance at the peak of each half-cycle, and thus the number of the alternating decay cycles in the spark is controlled. Such control leads to more uniform and reproducible excitation conditions.



V, voltmeter. L, inductance
C, Condenser. R, damping resistance
Fig. V-3. Feussner Circuit for spark source

In general, the spark source excites predominately ionic spectra. It is more reproducible and stable than the arc. Less material is consumed and consequently the concentration range over which it is applicable is higher than that of the arc. Since the heating effect is less than that of the arc, it is well adapted for the analysis of low melting materials. The spark source is also free from the troublesome cyanogen bands. However, the spark may strike to a particular spot on an electrode and thus give an unrepresentative indication of the concentration of substance being determined.

The spark source is readily adapted to the analysis of solutions. The solution, rendered conducting by the addition of hydrochloric acid, is allowed to flow over a lower electrode while a spark is struck to the electrode, or rather to the thin layer of solution above the lower electrode. A bundle of fine wires may also serve as the lower electrode and draw the solution up to the top of the bundle by capillary attraction.

Several types of spark sources have been proposed. Each has its special uses. A complete discussion will not be attempted here. The reader is referred to the more complete books on spectrographic analysis listed at the end of this chapter.

For the excitation of gases such as He, A, Kr, Ne, Xe, H_2, O_2, N_2, S_{vapor}, and Na_{vapor}, a gaseous discharge tube - that is, the common Geissler tube - is employed.

Spectrographs

Every spectrograph will have a dispersing medium, either a grating or a prism, a slit, and a camera or other recording device. These component parts will be discussed briefly at this point.

The spectral lines recorded are replica images of the slit. The slit should, therefore, be straight and have parallel and sharp edges to

2. Feussner, O., Arch. f. Eisenhüttenwesen, 6, 551 (1921).

avoid reflection from the edges. It should be kept clean and free from nicks since dust particles or imperfections will be reproduced in the images. The slit should be adjustable, preferably continuously so, and should also be bilateral, that is, both sides should open or close rather than just one side.

When using a prism and with some mountings of gratings, lenses are required to render the light parallel and to focus the light on the camera or recorder. Since the focal length of a lens varies with the wavelength, light of different wavelengths will be brought to focus at different distances from the lens. If the lens can be constructed from two or more different materials it can be made to bring all wavelengths to focus at the same distance; but in the ultraviolet region, where practically only quartz is available, this is not possible. The plate or film must then be tilted and curved somewhat to compensate for this characteristic of the lens. Lenses also show other errors such as spherical aberration which may require grinding of aspherical surfaces for correction or the use of only small lens apertures.

Prism Instruments

The chief distinguishing feature of the various spectrographs is whether they employ a prism or grating as the dispersing medium and in the particular type of mounting of that medium. Three common types of mountings for prisms - the Cornu, the Littrow, and the Wadsworth - are illustrated in Figs. V-4 to V-6. Glass and

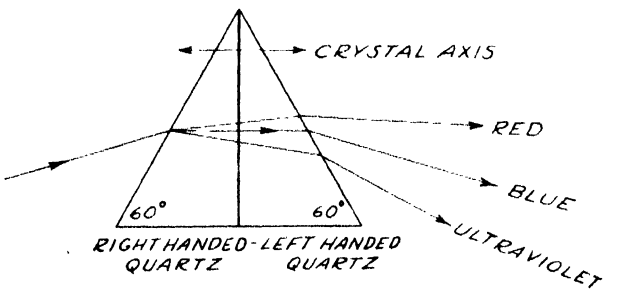


Fig. V-4. Cornu type prism mounting

quartz are the usual materials for prism construction in the visible and ultraviolet regions, respectively.

The Littrow mounting employs only one piece of quartz. Use of the Littrow mounting results in a compact instrument.

The Cornu mounting requires two pieces of quartz, one right-handed and one left-handed

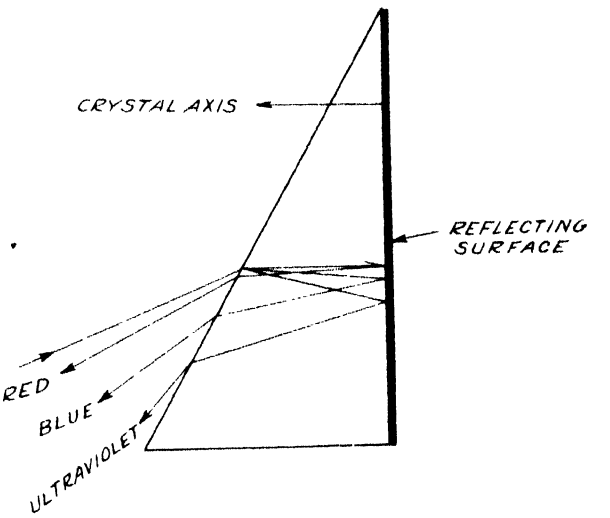


Fig. V-5. Littrow type prism mounting

piece. This is necessary since quartz possesses the property of rotating the plane of polarized light and will also separate an unpolarized beam into two beams, circularly polarized in opposite directions. Since the index of refraction for the two beams is different, two images would result unless two different types of quartz crystal are used or unless the beam is returned in an opposite direction through the crystal. Glass, because it is isotropic, does not show this effect and only one piece is required. It is used frequently in instruments of medium dispersion and in the cheaper instruments employing glass optics.

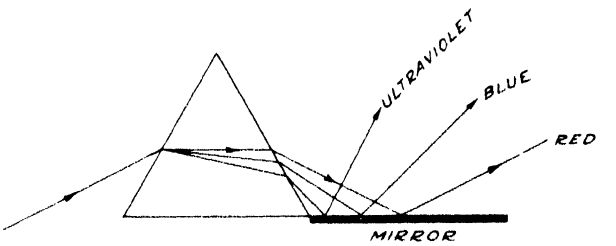


Fig. V-6. Wadsworth type prism mounting. The beam passing through the prism at the angle of minimum deviation (red, in this case) is parallel to the entering beam

The Wadsworth mounting gives a beam parallel to the entering beam which may be of some advantage in certain cases. It is sometimes used in the infrared region.

Other special types of prisms and mountings are used for special purposes such as constant

deviation or direct-vision spectroscopes.

The schematic optical diagrams and photographs of several prism instruments are shown in Figs. V-7 to V-11.

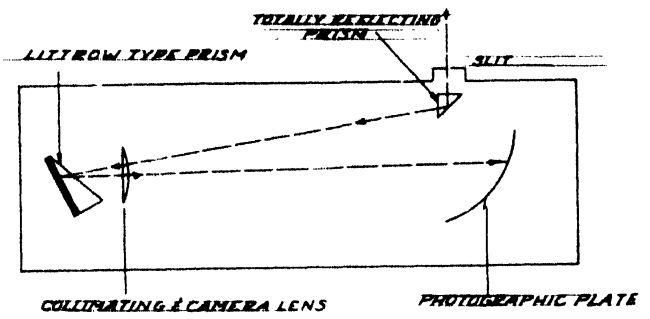


Fig. V-7. Diagram of the optical system of a Littrow type spectrograph

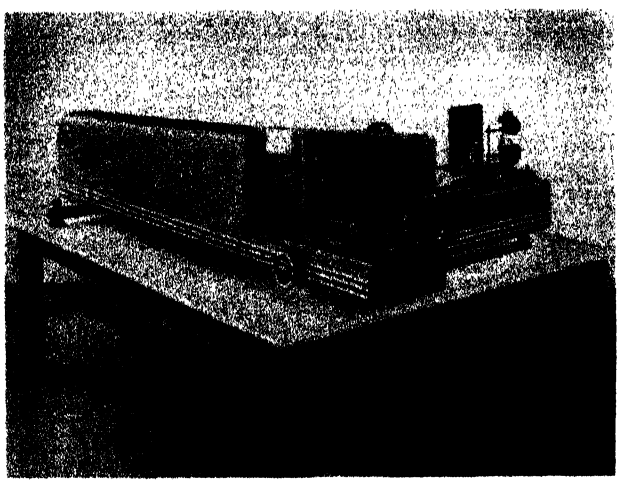


Fig. V-8. Large Littrow spectrograph (Courtesy of Bausch & Lomb Optical Co.)

Efficiency of Prism Instruments

The index of refraction of substances varies with the wavelength and over short ranges can be expressed by Hartmann's formula:[3]

$$n = n_0 + \frac{c}{(\lambda - \lambda_0)} \qquad (2)$$

where n = index of refraction;
λ = wavelength;
n_0, λ_0, and c = constants.

3. Hartmann, J., Astrophys. J., 3, 218, (1898).

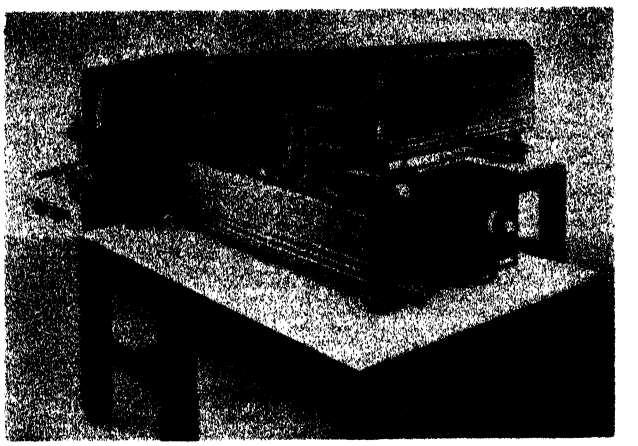


Fig. V-9. Large Littrow spectrograph and Illuminating Unit (Courtesy of Bausch & Lomb Optical Co.)

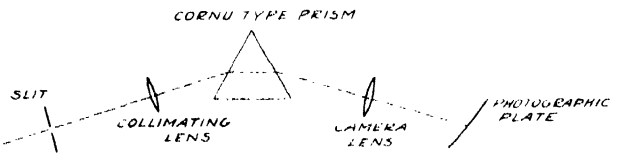


Fig. V-10. Optical Diagram of a Cornu type spectrograph

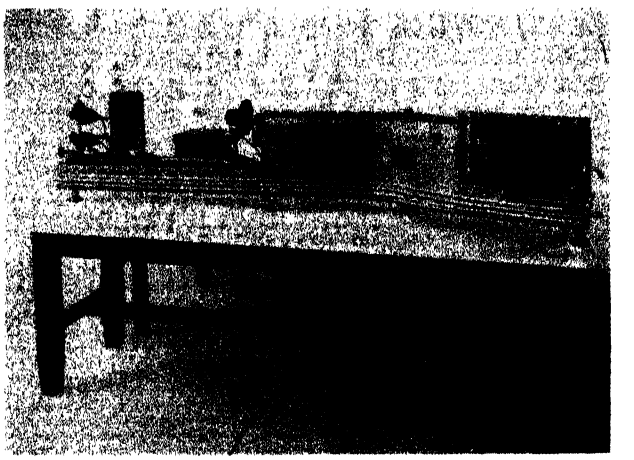


Fig. V-11. Medium quartz spectrograph, Cornu type (Courtesy of Bausch & Lomb Optical Co.)

The angular dispersion, the change in angle of the dispersed beam with a change in wavelength, is represented by D and is equal to $\frac{d\theta}{d\lambda}$. Prisms show greater dispersion at shorter wavelengths, that is, toward the ultraviolet region. The dispersion may also be conveniently represented as linear dispersion, $\frac{dx}{d\lambda}$, where x represents the distance in millimeters on the plate between two

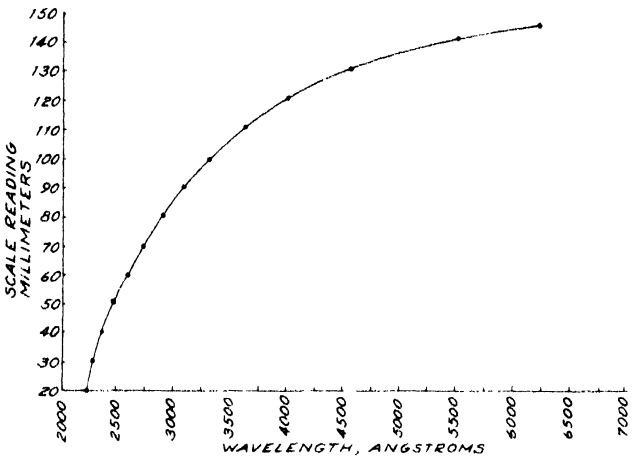


Fig. V-12. Typical calibration curve for Bausch and Lomb small Littrow spectrograph

lines $d\lambda$ apart. A typical curve relating wavelength to scale reading (in millimeters) for a Bausch and Lomb Small Littrow Prism Spectrograph is shown in Fig. V-12. This nonlinear dispersion of prismatic instruments causes some extra work in calculating the wavelengths of unknown lines. The determination of wavelengths is made either from a graph constructed for the instrument or by measuring the position of three known lines and the unknown line and employing the formula of Hartman in the form.

$$\lambda = \lambda_0 + \frac{c}{d_0 - d} \qquad (3)$$

in which λ_0, c and d_0 are constants.

The resolving power, R, indicates the ability of a spectrograph to resolve two spectral lines separated by wavelength $d\lambda$.

$$R = \frac{\lambda}{d\lambda} = t\frac{dn}{d\lambda} \qquad (4)$$

λ = the average wavelength of two lines just distinguishable from each other;
$d\lambda$ = the difference in wavelength of these two lines;
t = thickness of the base of the prism.
n = index of refraction

Since $\frac{dn}{d\lambda}$ remains nearly constant for most prism materials, the thicker the prism the greater the resolving power will be. Resolving power is also affected somewhat by the width and shape of the slit and by the other characteristics of the optical system.

Grating Instruments

A grating consists of a large number of parallel, equally spaced lines ruled upon a glass or metal surface. For most spectrographs the gratings are ruled on concave surfaces and are covered with a thin layer of evaporated aluminum. Some of the cheaper instruments employ replica gratings. These are made from original gratings by coating the original with a plastic and then stripping off the plastic. Many copies can be made in this manner.

When light is diffracted from a grating surface several "orders" of spectra are produced on both sides of the normal. The equation is

$$n\lambda = d(\sin i + \sin \theta) \qquad (5)$$

where n = "order" of the spectra;
λ = wavelength;
d = spacing between lines of the grating;
i = angle of incidence;
θ = angle of diffraction.

The light energy is divided into several spectra, only one of which is eventually employed. It is possible, however, to rule gratings in such a manner that as much as 80% of the energy will fall in any desired order. Such gratings are known as "echelette" gratings.

The common types of mountings of gratings are the Rowland, Paschen-Runge, Wadsworth, and Eagle. These are illustrated in Figs. V-13 to V-16. The Rowland mounting is so arranged that the film and grating are at right angles to the slit. The length of the arms is such that the three components all lie on the Rowland circle. The Rowland circle is a circle with radius of

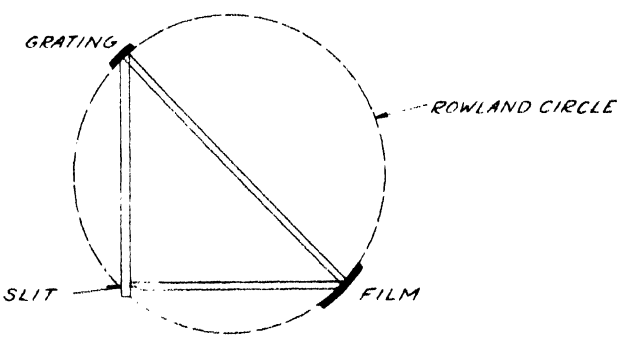


Fig. V-13. Rowland mounting for a concave grating

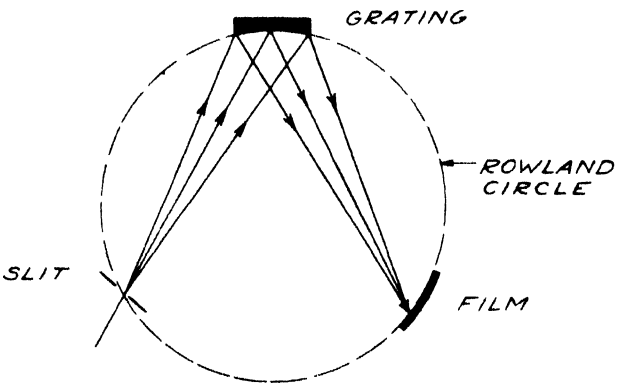


Fig. V-14. Paschen-Runge mounting for a concave grating

curvature half that of the grating itself. If the slit and grating lie on the Rowland circle, the images of the slit are brought to focus somewhere on this same circle.

The Paschen mounting requires a circular track for the camera, but movement of the camera from one region to another is relatively easy.

The Wadsworth mounting requires a mirror so that the grating may be illuminated by parallel light. The light gathering power of the arrangement is high. Furthermore, the arrangement is stigmatic, that is, light arising from horizontal lines and from vertical lines is brought to focus at the same distance from the grating. Most other grating mountings are astigmatic and it is

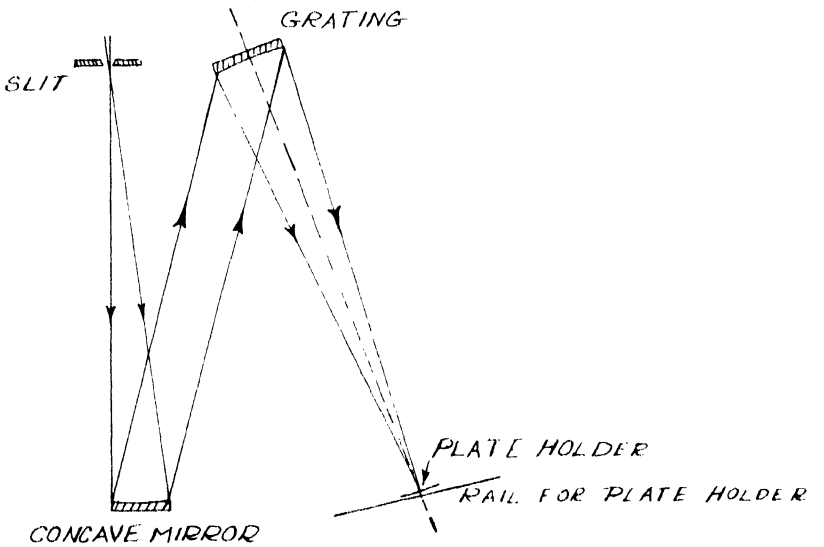


Fig. V-15. Wadsworth mounting for a concave grating

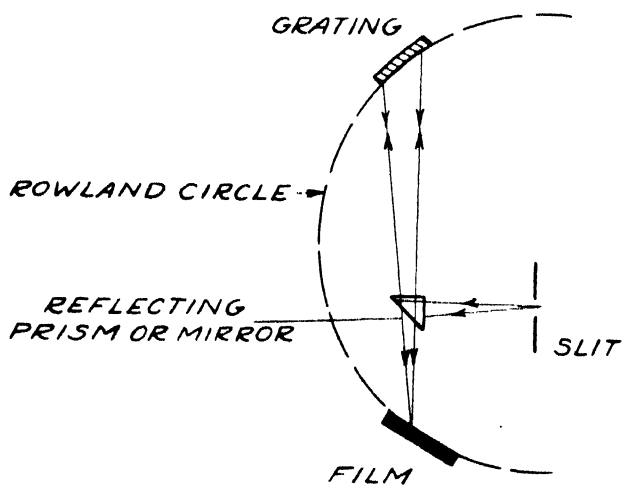


Fig. V-16. Eagle mounting for a concave grating

then necessary to find some position beyond the slit in which to place any device which would limit the length of the lines produced by the slit. There are two positions in an astigmatic mounting in which lines will be in focus at the camera, one position for vertical lines (the slit edges) and one position for horizontal lines (the limiting devices).

The Eagle mounting, or modifications thereof, is very popular in spite of the fact that rather complicated adjustments are needed for the film and grating. The astigmatism is slight in such a mounting.

Examples of commercially available spectrographs employing gratings are shown in Figs. V-17 to V-21. The Cenco instrument (Paschen-Runge mounting) is relatively inexpensive and has a dispersion of 16 Å/mm. The Applied Research Laboratories' 1 1/2 meter spectrograph (Paschen-Runge type) has a dispersion of 7 Å/mm.

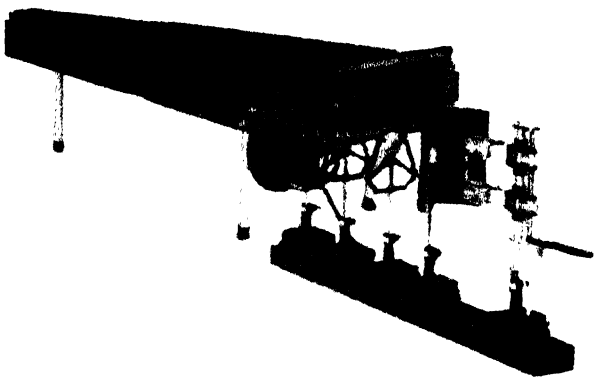


Fig. V-17. Cenco Grating Spectrograph (Courtesy of Central Scientific Company)

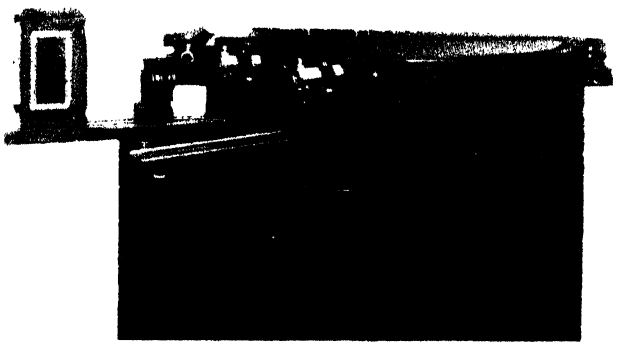


Fig. V-18. Applied Research Laboratories' 1 1/2-Meter Grating Spectrograph (Courtesy of Applied Research Laboratories)

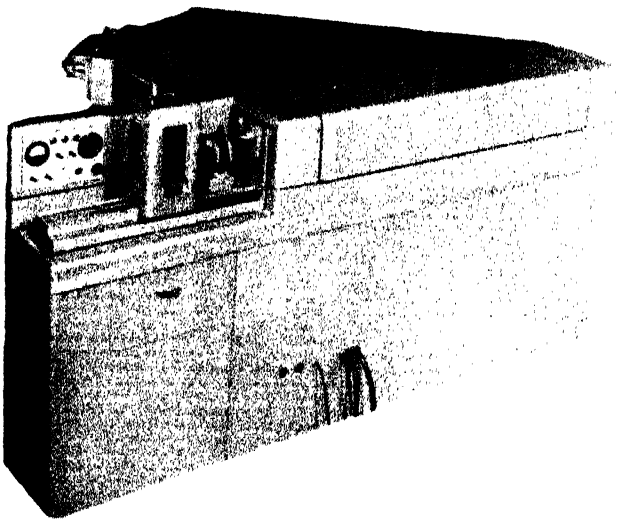
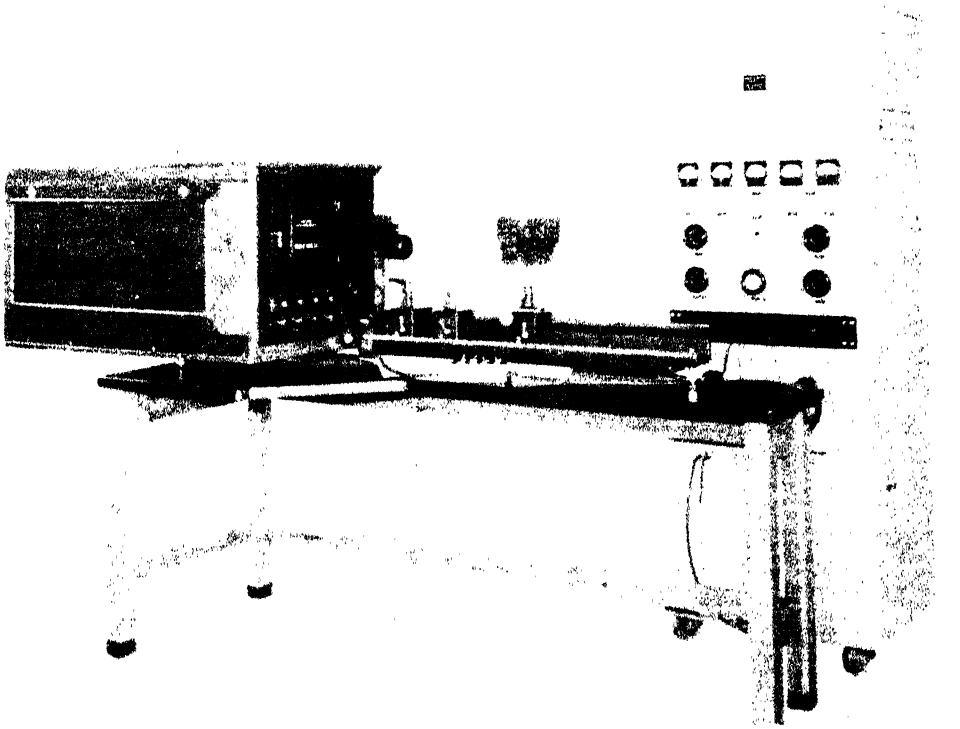


Fig. V-19. Applied Research Laboratories' 2-Meter Grating Spectrograph (Courtesy of Applied Research Laboratories)

Fig. V-20. Baird Associates' 3-Meter Grating Spectrograph with source power panel (Courtesy of Baird Associates)



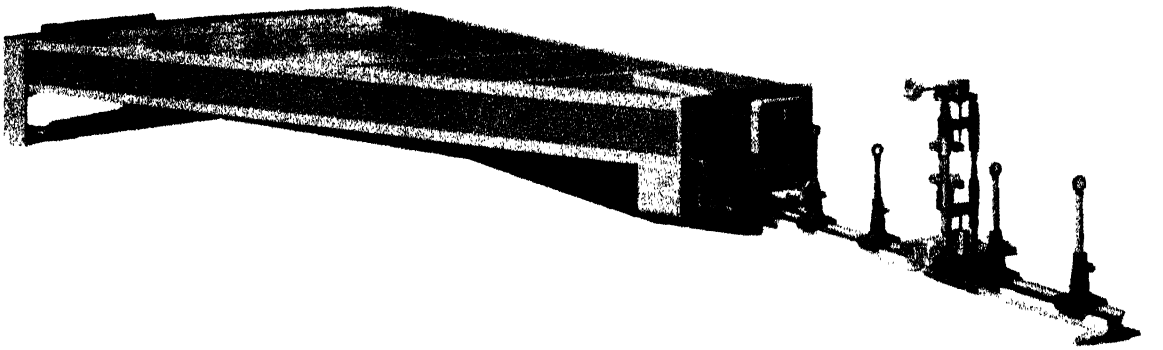


Fig. V-21. Jarrell-Ash Large Grating Spectrograph (Courtesy of Jarrell-Ash Co.)

or 4.6 Å/mm. in the first order depending on whether a grating with 24,400 or 36,600 lines per inch is chosen. The 2-meter model has a dispersion of 3.4 Å/mm. with the 36,600 lines lines per inch grating. The 3-meter spectrograph by Baird Associates (Eagle type) has a dispersion of 5 Å/mm. in the first order. The Jarrell-Ash large spectrograph (Wadsworth type) has a dispersion of about 5.0 Å/mm. with a 15,000-lines-per-inch grating or 2.4 Å/mm. with a 30,000-lines-per-inch grating.

Efficiency of Grating Instruments

The dispersion, both angular and linear, is defined in the same manner as that for a prism instrument. For a grating, however, the dispersion is constant or very nearly so and does not vary with wavelength as it did with a prism. The dispersion is said to be "normal." This is a decided advantage when it comes to identifying lines.

The resolving power of a grating, R, can be shown to be

$$R = nN \qquad (6)$$

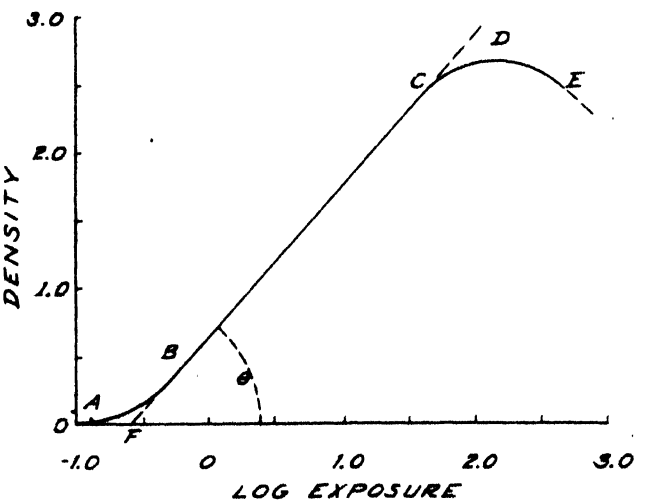
in which n is the order of the spectrum and N is the number of lines in the illuminated portion of the grating. Resolving power also depends upon the quality of a grating. A grating may show faint displaced images of lines, "ghost lines," due to imperfections in the ruling. It will also usually show some faint higher order spectra overlapping the desired spectrum.

The particular spectrograph to be used in any situation depends on the type of material and the nature of the work to be performed. For materials with fair amounts of iron, cobalt, nickel, manganese, uranium, chromium, and the like, an instrument with high dispersion is required since the spectra of these elements consist of a very great number of closely spaced lines. For alloys of aluminum, lead, tin, copper, silver, magnesium, etc., an instrument with dispersions of only 10-20 Å/mm. will suffice since only a few lines appear.

The Photographic Process

In all spectrographs except the recently developed recording instruments, the intensity of the lines is ultimately registered on a photographic emulsion. The nature of the photographic process is of considerable importance.

If one plots the density of a film as a function of the logarithm of the exposure, curves such as the one shown in Fig. V-22 result. It will be noted that there is a region, B-C, over which the optical density is directly proportional to the log



A, Threshold exposure. D-E, reversal region
B-C, Linear portion of curve. F, inertia of emulsion.

Fig. V-22. Characteristic curve of a photographic emulsion

of the intensity of exposure. This is the useful range of the film. The slope of this straight portion of the curve is known as the γ of the emulsion.

$$\gamma = \text{Tan } 0. \qquad (7)$$

High values of γ indicate a high degree of contrast and low values of γ indicate low contrast.

The density of a film can be measured by passing a beam of light through a clear portion of the film and measuring the intensity of the transmitted beam by a photocell. The beam is then passed through the blackened portion of the film and the intensity is recorded. The logarithm of the ratio of the intensity of light passing through the clear film and through the blackened film is the density. Three examples of commercial densitometers are shown in Figs. V-23 and V-24a.

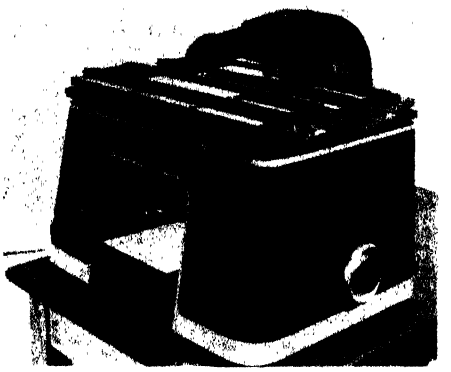


Fig. V-23. Jaco Projection Comparator Microphotometer (Courtesy of Jarrell-Ash Co.)

The shape of the characteristic curve of a photographic emulsion varies from emulsion to emulsion, with wavelength, and with the conditions of development. In order to determine the curve for any given emulsion, it is first necessary to standardize the conditions of development, that is, the time, the type of developer, the temperature, etc. A step-wedge transmitting known relative intensities of light through the various steps may then be placed directly on the film and the film exposed through the wedge. After development the densities of the steps are measured and plotted against the known intensities. In order to calibrate at several wavelengths it is better to place the wedge in front of the slit of the spectrograph and expose with a metallic arc, such as a copper arc. Each line will then show a reproduction of the wedge.

Instead of a wedge or a series of filters with known transmittancies, a rotating step-sector disc or a log-sector disc (Fig. V-25) may be placed in front of the slit. The different parts of the lines will show definite, graduated intensities depending upon the construction of the sector. Photographic

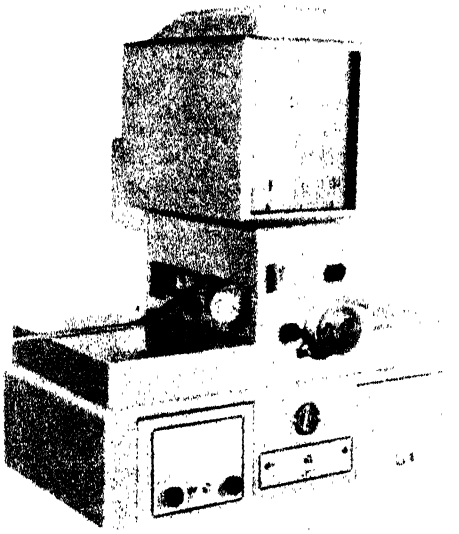


Fig. V-24. Applied Research Laboratories Densitometer-Comparator (Courtesy of Applied Research Laboratories)

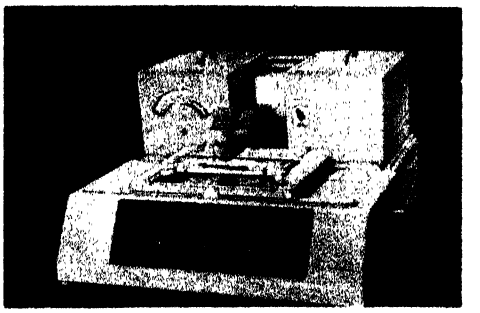


Fig. V-24a. Bausch & Lomb Densitometer (Courtesy of Bausch and Lomb Optical Co.)

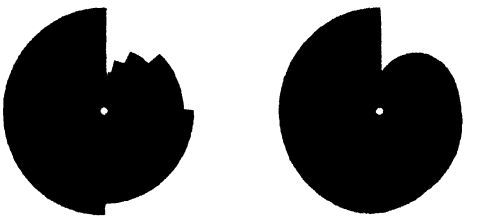


Fig. V-25. Step-sector Disc and Log-sector Disc

emulsions, however, show what it known as an intermittancy effect, that is, several short exposures may not produce the same effect as one long exposure. In other words, the relationship

$$E = It \qquad (8)$$

(where E = exposure; I = intensity; t = time of exposure) breaks down if intermittent exposures are

employed. If the frequency is high, this effect may be negligible, however. Sectors are run by high-speed motors.

The sensitivity of photographic emulsions to light of different wavelengths can be varied by the addition of certain dyes when the film is prepared. Thus, panchromatic film is sensitive into the red region of the spectrum, and orthochromatic film is sensitive into the green and yellow regions. Ordinary emulsions are sensitive in the ultraviolet and blue regions only. If the lines at long wavelengths are not to be measured, ordinary film should be used. Ordinary film can be observed during development with red light, whereas panchromatic film must be developed in nearly total darkness.

Qualitative Identification

The elements present in a sample can be determined by comparing the spectrum of the unknown with that of pure samples of the elements or by measuring the wavelengths of the lines and looking up the corresponding elements in tables. If only certain elements are being sought, the spectra of these elements may be taken on one film along with the spectrum of the unknown. It is then easy to see when a match is obtained.

Those lines of each element which are the last to disappear as the concentration of the element is gradually decreased are known as R.U. (raies ultimes) or persistent lines. These are the lines most useful in detecting small concentrations of impurities. A. Hilger in London prepares a powder containing more than 50 elements in such concentrations that only the R.U. lines of most of the elements appear in the arc spectrum. An identified spectrum of this powder taken on each spectrograph is a useful aid in identification of elements.

The wavelength of unknown lines may be determined by linear interpolation between lines of known wavelengths if the dispersion of the instrument is "normal." For prismatic dispersion, the formula of Hartmann (equation (3)) must be employed. Many instruments have wavelength scales which may be impressed on the film. Such scales are useful for rough identification of the wavelengths of lines.

For exact measurements of the distances of lines on a film, a magnifying glass with a built-in scale is useful. For distances greater than a few millimeters, a measuring microscope is useful.

There are many tables available which list the wavelengths of the spectral lines and the corresponding elements. Many of these tables are listed in the selected references at the end of this chapter. Once an element is definitely located by identification of three or more lines, the tables which list the lines under each element are useful in eliminating the remainder of the lines due to that element before proceeding with the identification of the second constituent, etc.

Quantitative Analysis

Early workers in spectrography attempted rough estimations of the concentration of elements in various ways. Hartley[4] correlated the concentration of solutions with the number of lines appearing in the spark spectrum.

DeGramont[5] and later Meggers, Kiess, and Stimson[6] employed a series of standard electrodes with known concentrations of the substance to be determined. Spectra of the various standards and of the unknown are photographed alternately on the same plate and under the same conditions. The concentration of the desired constituent can then be estimated by comparing the blackening of the lines of this constituent with the same lines in the standards. Photometric or simply visual comparison of blackening of the lines is possible. The accuracy depends on the number of standard samples available and on the ability to maintain constant excitation and exposure conditions.

In the above-mentioned methods and in any procedure that depends on the measurement of the intensity of only the lines of the unknown element, the excitation conditions, the time and nature of the exposure, and the conditions of development must all be carefully controlled. In order to eliminate the effect of variations in these factors, the modern methods of spectrographic analysis measure the intensity of an unknown line relative to that of an internal standard line. The internal standard line may be a weak line of the main constituent or it may be a strong line of some material added in a definite concentration to the sample. The ratio of the intensities of these lines, the analysis line and the internal standard line, will be unaffected by exposure conditions and development conditions. Gerlach and Schweitzer[7] were the first to propose this method of "internal standards."

4. Hartley, W. N., Phil. Trans. London, 175, 326 (1884).

5. DeGramont, A., Compt. rend., 159, 6 (1917); 171, 1106 (1920).

6. Meggers, W. F., Kiess, C. C. and Stimson, F. S., Bur. Standards Sci. Paper, 444 (1922).

7. Gerlach, W. and Schweitzer, E., "Foundations and Methods of Chemical Analysis by the Emission Spectrum," Adam Hilger, Ltd., London, 1929.

In order that variations in the excitation conditions shall not affect the relative intensities of the two lines, it is necessary that the two lines constitute what is known as an "homologous pair." Such pairs are lines that respond in the same way to changes in excitation conditions. Both lines always arise from the same type of excitation, that is, atoms or ions. Homologous pairs may be selected by experiment or be chosen on the basis of recommendations of others recorded in the literature. A "fixation pair" of lines is a pair of lines which change intensities quite differently with variations in the conditions of excitation. Such a pair of lines is sometimes observed as a check as to whether the excitation conditions remained constant.

Gerlach and Schweitzer[7] prepared tables listing homologous pairs of lines which had equal blackening at given concentrations of the desired element. Such a table for the determination of cadmium in tin is shown in Table 1.

TABLE 1. HOMOLOGOUS PAIRS FOR DETERMINATION OF CADMIUM IN TIN

Cadmium Line Å	Tin Line Å	Equal Intensity at Cd concentration
3404	3331	10
3404	3656	2
3404	3142	1.5
3404	3219	0.5
3466, 3468	3656	0.3
3611, 3615	3656	0.2
3404	3224	0.1
3466, 3468	3224	0.05
2288	2282	0.01

This method suffers from the defect that only definite limited steps are available.

The most obvious and the best method of comparing the intensities of the unknown and the internal standard line is to measure the density of the two lines on the film or plate by a densitometer. The intensity of the light striking the plate to cause the two lines is then calculated by means of the characteristic curve for the emulsion under the chosen conditions. Either the ratio of the intensities of the homologous pair of lines is plotted against concentration, or the log of the ratio is plotted against the log of the concentration. Either plot should result in nearly a straight line, since intensity of light is proportional to the concentration of the responsible atom or ion. A less precise method would be to plot the ratio of the densities of the lines directly against the log of the concentration, assuming, of course, that one is working on the strictly straight-line portion of the characteristic curve of the emulsion.

If a densitometer is not available, there are other methods of comparing the relative intensities of two lines. If a step-sector or a log-sector is run in front of the slit during the exposure, the resulting lines will have different lengths. The strong lines will be long, since even at small exposure times sufficient light will reach the film to cause visible blackening. On the other hand, the weak lines will be short. A measurement of the length of the lines indicates the intensity, thus:

$$\log c \text{ is proportional to } \log I \text{ or } D \qquad (9)$$

and if the sector is logarithmic, that is,

$$h \text{ is proportional to } \log I \qquad (10)$$

then,
$$h \text{ is proportional to } \log c. \qquad (11)$$

Actually the difference in height of the internal standard and unknown lines is plotted against the logarithm of the concentration. A nearly straight line should result (see Fig. V-26). The main difficulty with this procedure is in determining the

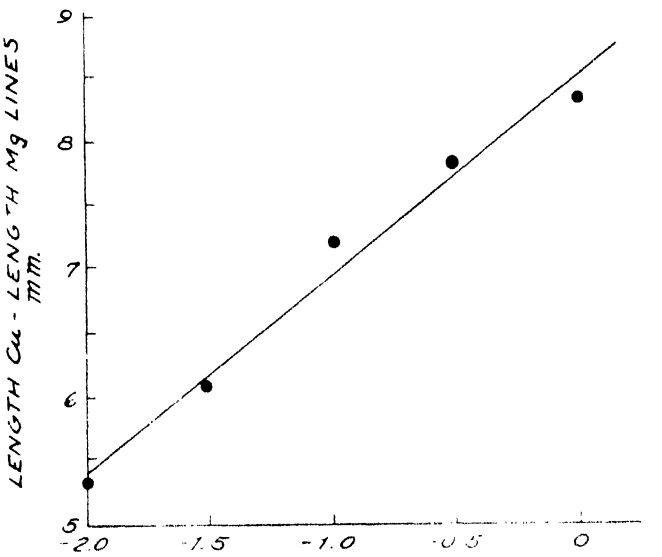


Fig. V-26. Example of working curve, log-sector method. Determination of copper in an alumina-silica mixture. Magnesium, 1%, added as internal standard. Lines compared: Cu 3274 and Mg 2852

exact length of the lines. It is very difficult to judge just when a line disappears.

The step-sector and photometric measurement of density methods can be combined for very precise work. If a step-sector is used, the densitometer can be used to measure the densities of the two lines at steps where the two lines are of nearly equal densities. The densitometer measurements are more precise when the densities are nearly equal. Since the ratios of intensities of the various steps are accurately known one can easily calculate the original intensities of the lines.

In any case a series of several standard samples must be run to establish points on the "working curve." Once this working curve has been established, similar unknown samples can be quickly analyzed. A new working curve must be established for each type of material. The presence of elements not originally present in the standard from which the working curve was established will usually affect the curve.

Recording Spectrographs

Most of the inaccuracies and disadvantages of the photographic emulsion as a recording device can be eliminated by substitution of phototubes, especially photomultiplier tubes, and suitable amplifying and recording devices. Several different schemes have been described. The A.R.L. quantometer shown in Fig. V-27 employs photomultiplier tubes and amplifying and counting devices to measure the intensities of the lines. One tube always monitors an internal standard line. When this latter recorder has made 500 counts, the whole spectrograph is automatically shut off. By using standard samples and varying the sensitivity of the counting devices, the tapes showing the intensities (number of counts) of the lines of the elements to be determined can be made direct-reading in percentage. An analysis of a metal alloy for as many as eleven constituents can be completed in about 45 seconds. The precision and accuracy are greater than in the older methods employing photographic recording but the sensitivity is somewhat less. The commercial instruments, are, however, several times more expensive than the older spectrographs.

Measurement of Absorption Spectra

If one uses a continuous light source or a source with many lines such as the iron arc, the light may be passed through a photometer and onto the slit of a spectrograph. Two spectra, one of light passing through the solvent and one through the solution, are recorded at each exposure. Several exposures are taken decreasing the light through the solvent beam by a definite amount each time. After the plates are developed, one can measure the wavelengths at which each exposure shows equal blackening of the

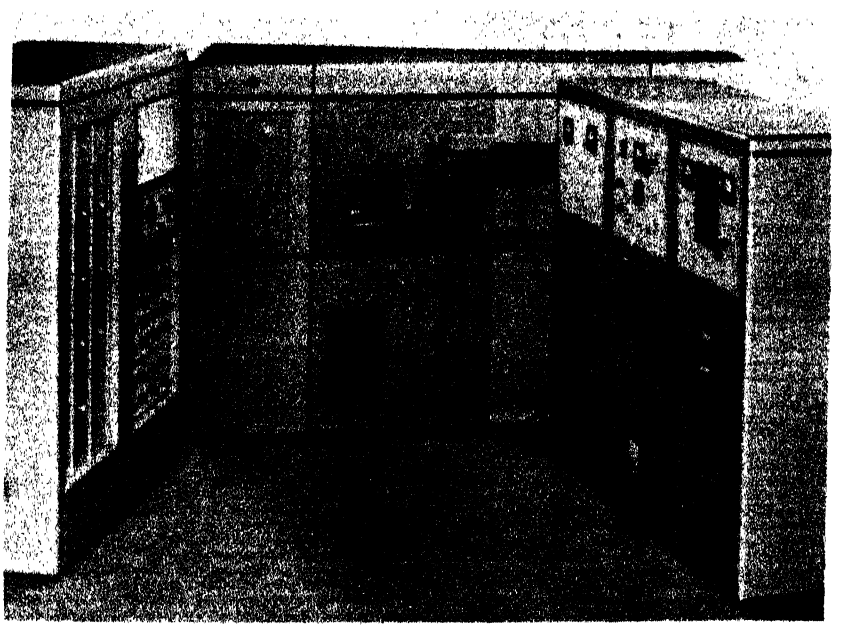


Fig. V-27. Applied Research Laboratories Quantometer (Courtesy of Applied Research Laboratories)

solvent and solution spectra. If one knows the amount of light removed from the solvent beam in each exposure, it is then possible to plot wavelength against optical density and thus determine the absorption curve of the solution. This method is more tedious than that using a modern spectrophotometer, but it does have the advantage that very narrow bands of light can be employed effectively and, therefore, narrow and sharp absorption bands will not be overlooked.

RAMAN SPECTROGRAPHY

The theory of Raman spectra is closely related to that of infrared spectra and perhaps should have been discussed in the previous chapter. However, since spectrographs are commonly employed to register the Raman effect, the discussion has been postponed until this point.

When a photon of rather high energy, as, for example, one in the visible or ultraviolet region of the spectrum, strikes a molecule in its ground state, it may raise the molecule to a higher rotational-vibrational state. The energy required for the excitation is rather small. The remaining energy of the photon is decreased by this amount, however, and the photon will proceed from the collision with the molecule with a reduced frequency. Since there are a few molecules in a liquid at ordinary temperatures in an excited rotational-vibrational state, it sometimes happens that a photon will collide with an excited molecule and will pick up energy as the molecule returns to the ground state. Thus the photon will have an increased energy content and a correspondingly higher frequency after the collision. The normal process, a decrease in energy of the photon, results in lines known as Stokes lines and the reverse process gives the so-called anti-Stokes lines. The above phenomena can be represented by the equations:

$$\Delta E = h\nu_1 - h\nu_2 = h\Delta\nu \qquad (12)$$

$$\Delta E = (E_g + E_{vib.}) - E_g \qquad (13)$$

or $$h\Delta\nu = E_{vib.} \qquad (14)$$

where E_g = energy of ground state;

$E_{vib.}$ = energy of excited vibrational state;

ν_1 = frequency of incident light;

ν_2 = frequency of Raman line;

$\Delta\nu$ = "Raman shift."

The shift in frequency of the lines is seen to be proportional to the vibrational-rotational energy involved in the transitions. Thus Raman shifts should correspond to actual absorption bands appearing in the infrared spectrum of a substance - both being due to shifts in the rotational-vibrational levels of the molecule. The Raman effect is, therefore, just as characteristic of a substance as is the infrared spectrum.

The requirement for an infrared absorption band to appear was that there be a change in the dipole moment of the molecule as it becomes excited. The requirement for the appearance of the Raman effect is that there be a change in polarizability of the molecule. Since the two requirements are somewhat different, on occasion lines may appear in one spectrum and not in the other, or lines may appear in both spectra. The infrared and Raman effects are, in a way, partially complementary to each other.

To observe the Raman effect, the apparatus is arranged as in Fig. V-28. The mercury arc furnishes an intense source of radiation, and the filters can be used to isolate a single line. The spectrograph employed should have a high light gathering power since the Raman effect is weak. The resulting spectrogram will show an intense center line due to the simple scattering of some of the original radiation and will show the Stokes, or Raman, and anti-Stokes lines as faint lines on either side of the intense center line. The wavelength or frequency of these lines can be measured, and, from the known wavelength of the incident radiation, the displacement $\Delta\nu$ is calculated. Since the intensity of the Raman lines increases rapidly as the wavelength of the incident lines decreases, it is preferable to use the lines of the mercury arc of shorter wavelength.

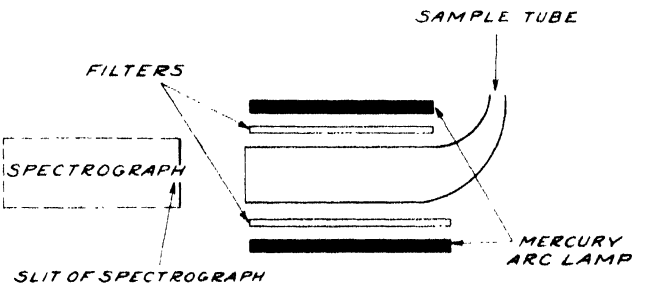


Fig. V-28. Experimental arrangement for observation of the Raman effect

For qualitative purposes the procedure is much the same as in infrared work. The spectrum of

the unknown is compared with that of pure compounds until a match is obtained. The Raman effect is much less sensitive than the infrared effect and thus impurities cannot be detected as well by the Raman spectrum as by the infrared absorption spectrum. The time required to photograph the Raman effect depends on several factors, such as the specific nature of the material, the intensity of irradiation, the spectrograph employed, etc.; but, in general, the time required is longer than that required for recording infrared spectra.

Quantitatively, the intensity of the Raman lines is proportional to the concentration of the material, provided that all other variables, such as intensity of irradiation, time of exposure, etc., are kept constant. In actual practice it is advisable to measure the intensity of the Raman lines relative to that of an internal standard substance. Carbon tetrachloride makes a good internal standard since it shows quite intense Raman lines. It can be added to the unknown samples in a definite concentration before each exposure. One difficulty frequently encountered in the use of the Raman effect is caused by the presence of fluorescing materials in the unknown samples. Such materials will produce a general background on the film which may easily obscure any Raman lines. The samples must be carefully freed from all fluorescing substances.

LABORATORY WORK WITH SMALL SPECTROGRAPHS

General Instructions for Operation of the Cenco Grating Spectrograph with Log Sector

1. The grating adjustment should not be changed. Also the slit position adjustment should not be changed. This adjustment is accomplished by the lower thumbscrew near the slit and this screw, therefore, must not be moved. These adjustments have been properly made by the instructor and if there is any doubt concerning them, consult the instructor.

2. A fixed slit may be used in conjunction with the log sector; however, it is not necessary, and as good, if not better, results can be obtained without it. If the fixed slit is to be used, it is attached by the screws on the instrument case outside of the movable slit. The adjustable slit is opened as wide as possible, using the upper thumbscrew with calibrated dial.

If the fixed slit is not to be used, open the adjustable slit only about 20 to 40 divisions from the completely closed position. Take care not to force the slit closed at any time. Forceful closing might injure the sharp edges of the slit.

Illuminate the slit with parallel light. This is accomplished when the spherical lens is placed at a distance from the arc equal to the focal length of the lens used.

Adjust the position of the fixed slit, if used, until light passes through both slits. Use any bright light or a metallic arc to observe this. The cover on the instrument is removed and the light observed by holding a white card in the light path. The shutter is operated by the button on the right side of the instrument.

3. Mount the sector disc so that the disc is as close to the slit as possible. Adjust the height so that about 2 mm. of the upper end of the slit is always illuminated or until about 2 mm. of line remains always visible when a frosted glass is held on the camera track and the sector is rotated so as to cut out the maximum amount of light. The sector should be mounted so that its sharp, vertical cutoff is parallel to the slit at the moment it passes in front of the slit.

4. Remove both slotted masks from the spectrograph (in front of the camera holder). Adjust the position of the arc so that light falls on the grating. Observe the position of some spectral lines by holding a frosted glass on the film track. The light source is adjusted until the lines are uniformly bright along their whole length and are as long as the opening in the spectrograph (about 14-16 mm.). This is the most critical part of this experiment and care should be taken to make the adjustment carefully. Mark the height of the arc carefully by noting the distance above the lower electrode holder. Henceforth do not move the lower holder.

The sector is turned so that as much of the slit as possible is illuminated while making these adjustments.

5. Load the film in the camera in a totally dark room. Place the film in the holder so that the emulsion side will be exposed. The film curls toward the emulsion side. Some films are notched so that, if the notch is at the top right facing into the spectrograph, the emulsion will be in the correct position.

6. Place the camera in the instrument. Close the cover on the spectrograph, close the shutter, and pull out the dark slide from the camera.

7. Place a cupped electrode (drill a hole about 5 mm. x 8 mm. in a 2- or 3-inch piece of graphite) in the lower, positive electrode holder and a 2 1/2-inch graphite rod turned down to a blunt point in the upper holder. Adjust the position according to the result obtained in paragraph 5 above.

8. Fill the cup with the material for the first exposure. A little powdered graphite on top of the filling will make the arc easier to control. Cyanogen bands are kept to a minimum by using low current or medium current positions on the rheostat. If the

arc does not strike easily it can be started by drawing a graphite rod across the joint.

9. The sector motor is started. The motor operates on 110 volt, A.C. only.

10. The first exposure is taken with the camera at position 3; the second exposure, at position 11.

11. Each exposure should consist of 5 parts of 10 to 20 seconds each, refilling the electrode cup after each part. It is advisable to try one film for correct exposure first (try 3 x 10 seconds and 5 x 15 seconds). Estimate from this film the best exposure time and expose all others similarly. The films may be stored in a lightproof box until all are ready and then all may be developed at the same time.

12. If a series of standards is to be run, the same electrode may be used for the series, provided that the lowest concentrations are run first. Clean the electrode each time. If liquids are used, evaporate 0.1 ml. in the cup of the electrode by placing the electrode in a drying oven at about 93°C. for 30 minutes. Use a separate electrode for each sample. The electrode may be dipped in redistilled kerosene before adding the liquid to make the electrode waterproof.

In special cases the material may be arced using copper or silver electrodes as holders or the sample itself may form the electrodes.

13. Replace the dark slide in the camera. Remove the camera, open in a totally dark room and develop, fix, wash, and dry the film in the usual manner. DK19 developer requires about 4 minutes at 20°C. Fix 20 minutes or twice the time required to clear the film. Wash at least 1 hour in running water. Rinse finally with distilled water and dry.

14. Measure the length of the lines of the unknown and standard substance using the spectrum viewing box and the measuring magnifier. Plot difference in heights of the lines as ordinate against log per cent concentration as abscissa. Also plot against per cent concentration as abscissa. The first plot should give a straight line.

15. Treat the unknown sample in the same way as the standards, using a fresh graphite electrode. Measure the heights of the lines and read the percentage of the unknown from the working curve. Hand in all data with the report.

16. For spectrograms without the log sector the fixed slit is removed and only the adjustable slit is used. As fine a slit as possible, without making the exposure time unduly long, is used. Focus the arc on the slit for qualitative work and use the wedge diaphragm in front of the slit to eliminate the images from the hot ends of the arc. For quantitative comparisons, use parallel light to illuminate the slit.

Seven exposures can be made on one film if the slotted metal mask with a 4 mm. opening is inserted in the spectrograph just in front of the camera. Fourteen exposures can be made if the 2 mm. mask is used.

Determination of the Concentration of a Substance. Obtain an unknown sample and a series of standard samples from the instructor. The instructor will indicate the element to be determined and the internal standard or standards which have been added to the samples. Photograph each sample using the procedure described above; two samples are recorded on each film. Identify the main lines appearing on the spectrogram and select several homologous pairs by reference to the tables in Brode.[8] Measure the height of a pair of homologous lines and construct a working curve. It may be necessary to try more than one pair before a suitable one is found. It may also be necessary to construct two working curves using two pairs for low and high concentrations of the unknown. The exposure should be sufficient to record the lines on the film but not so long that the lines are more than 13 or 14 mm. in length. Measure the height from some common point for all lines, that is, from the line made by the edge of the sector.

As a help in identifying lines it is well to move the last film up to position 10 after the last exposure and turn the sector to obscure the maximum amount of the slit. Record a 20-40 second exposure of a standard pure substance, such as a copper arc. This exposure will appear in a 2 mm. zone immediately below the last exposure.

For rough quantitative work the sector may be dispensed with. Record a series of standards and the unknown on the same film so that an exposure of the unknown will be interposed between two standards, thus, standard 1, unknown, standard 2, standard 3, unknown, standard 4, etc. The unknown concentration is determined by comparing visually the blackening of the lines of the constituent to be determined. The exposures must be the same for standards and unknown if this method is to be used. A table of pairs of homologous lines showing equal blackening at given concentrations may also be prepared and used.

The dispersion of a grating instrument is linear with wavelength and is almost exactly 400 Å per inch (16 Å per mm.) for the Cenco instrument. A rule graduated to 40 parts per inch (an architect's rule) is very useful in measuring wavelengths. A measuring magnifier can be used for accurate interpo-

8. Brode, W. R. "Chemical Spectroscopy," 2nd Edition, John Wiley & Sons, Inc., New York, 1943, pp. 400-610.

lations of the position of an unknown line between known lines. The tables of wavelengths of lines in Brode[8] and the handbooks are very useful.

General Instructions for Operation of the Bausch and Lomb Small Quartz Spectrograph[9]

1. Place a small amount of the material to be investigated in the core of a carbon electrode which is then placed in the lower holder of the arc. The lower electrode is made the positive electrode. The core may be 4 or 5 mm. deep and can be produced by a machine drill. The upper electrode is sharpened to a blunt point by a pencil sharpener.

2. Turn the ballast resistance to the "low" position and strike the arc by running the carbons together and then separating them by a few millimeters. If the arc does not strike in this manner it can usually be started by drawing a third carbon across the junction of the two electrodes. If the arc consistently goes out when the separation is not more than 7-8 mm., turn the resistance to "Med." and try again. Metal arcs are struck in the same manner but only "low" should be used. With iron arcs it is preferable to have the lower electrode the positive one, but for other metals the polarity is not of much importance.

3. Remove the plate holder by pushing the lock lever at the bottom to the left and then sliding the holder upward out of the gibs. The scale must be down (lever horizontal) before removing the holder.

4. Set the quartz lens so that an image of the source is secured on the slit with a magnification of three or four times. The lens will be closer to the light source than to the slit! The magnification is not critical; the image should be considerably larger than the slit.

5. Remove the lens, introduce the 20 micron slit into place, and adjust the source horizontally and vertically until its image is centrally located in the rectangular aperature of the spectrograph lens. To observe the centering, the shutter should be opened (pressed down) and the lens viewed by placing the eye as convenient as possible to the plane where the photographic plate will be. Under these conditions the spectrograph lens will not be filled with light; instead, a rather hazy dispersed image of the source will be seen.

6. Replace the condenser lens and adjust it to produce a sharp image of the source on the slit. Do not disturb the position of the source. The spectrograph lens will now be completely and evenly filled with light.

7. Choose the proper slit to be used for the conditions. The smallest slit gives the maximum resolution but requires longer exposures. If the source is weak (if the constituent is in very small concentration), a larger slit should be used.

8. Load the plate holder by placing it upon a flat surface with the metal plate downward and the dark slide closed. Release the catch and open the back. Place the plate with emulsion side down on the curved guides. Close the back and snap the catch in place.

9. Be sure the scale is down (the lever horizontal) before replacing the holder. Replace the holder in the instrument and lock to the elevating screw by pushing the lock lever to the right.

10. Be sure the shutter is closed (up).

11. Pull out the dark slide in front of the plate.

12. Adjust the plate to position 0, hold the scale against the plate by turning the lever down, and press the button on the base of the instrument for about 1 or 2 seconds. This registers the scale on the plate. Lower the scale.

13. Adjust the plate to position 1, start the arc, and expose the plate by depressing the shutter button for the required length of time. Record all details.

14. Adjust the plate to position 2 and take the second exposure. Proceed in the same manner until all exposures are taken.

15. Replace the dark slide and then remove the plate holder.

16. In the darkroom, remove the plate and develop and fix in the usual manner. D-19 developer requires 5 to 8 minutes. Wash 30 seconds in a short-stop bath containing 2 ml. of glacial acetic acid in 250 ml. of water. Fix for 10 minutes or for twice the time required to completely clear the plate. Wash in water for 15 to 20 minutes and then wipe with a soft sponge or cotton pad and allow to dry.

17. When dry the plate can be examined with the aid of the viewing box and magnifier.

18. Always replace the plate holder on the instrument and cover the instrument before leaving.

Qualitative Analysis

The unknown may be either a mixture of salts or an alloy. The elements to be sought for will be specified by the instructor. Use Eastman Process Pan plates if lines above 550 mμ are necessary for comparison; otherwise use Eastman 33 plates.

Take the spectra in the following order:

0. Scale
1. Standard (usually copper)

9. Adapted from the instruction manual furnished by Bausch and Lomb Optical Company.

2. Substance sought for
3. Unknown
4. Second substance sought for
5. Third substance sought for
6. Unknown
7. Fourth substance sought for.

At least three lines must be positively identified as coinciding in the substance sought for and in the unknown to be sure the element is present.

The wavelengths of the lines present could also be determined with the help of the lines of the standard substance. The unknown elements are then identified by reference to wavelength tables such as those of Brode,[8] Harrison,[10] Twyman and Smith[11] and the various handbooks.

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CHAPTER VI

X-RAY DIFFRACTION METHODS

The X-ray diffraction procedure furnishes a rapid, accurate method for the qualitative determination of the crystalline phases present in a material. Sometimes it is the only method available for determining which of the possible polymorphic forms of a substance are present. One can also determine which materials are present in such mixtures as KBr + NaCl, KCl + NaBr, KCl + KBr + NaCl + NaBr, etc., where chemical analysis would show only the ions present and not the actual state of combination. The presence of various hydrates will also be indicated. Although quantitative analyses by X-ray diffraction are also possible, they will not be discussed in this book.

Origin of X-Rays. When a rapidly moving electron impinges on an atom it may knock an electron completely out of one of the inner orbits of that atom. When electrons from the outer orbits of this unstable ion fall to the vacant inner orbit, the difference in energy is emitted as X-rays. X-rays are a form of radiant energy with very high energy or short wavelength. The wavelengths are of the order of a few tenths to several angstrom units.

If the vacant orbit is the K orbit, or the innermost one, then the X-rays produced will have very short wavelengths and are known as the K lines. Two closely spaced lines, the K_α and K_β lines, result. Actually each of these lines is a closely spaced doublet resulting from electrons falling from the L (second) and M (third) shell to the K shell. Other lines may appear as the electrons jump from shells beyond L and M to the K shell. If the vacant orbit is the L orbit, then the L lines result, etc. As the atomic number of the target element increases, the energy of similar X-ray lines increases and the wavelengths correspondingly decrease. The relationship between atomic number, Z, and frequency, ν,

$$\nu = K (Z-\sigma)^2 \qquad (1)$$

was discovered by Moseley and is known as Moseley's law. K and σ are constants in the above equation. In addition to these characteristic lines associated with each element, a much fainter continuous spectrum is produced. The minimum wavelength in angstrom units, λ_0, of this continuous spectrum is determined by the accelerating voltage, V, on the tube, thus:

$$\lambda_0 = \frac{300\ hc}{Ve} = \frac{12{,}400}{V} \qquad (2)$$

If X-rays should pass through other matter, they will be absorbed as is ordinary light. The relationship for absorption of X-rays is:

$$I = I_0 e^{-\mu l \rho} \qquad (3)$$

where I = emergent intensity of the beam;
I_0 = incident intensity of the beam;
μ = mass absorption coefficient;
l = length of path through the absorbing material;
ρ = density of absorbing material.

The mass absorption coefficient, μ, depends upon the wavelength of the X-rays and upon the absorbing material. It is independent, however, of the physical or chemical state of the absorbing material. As the energy of the X-rays impinging on a substance becomes greater, μ decreases until an energy is reached which is high enough to cause an electron to be cast out of an inner shell of the absorbing element. At this value of the wavelength of the X-rays, μ increases sharply. It is possible to find elements which will have strong absorption for the K_β X-ray lines from a certain target but will have rather weak absorption for the K_α lines. Thin films of these elements serve as filters to make the desired X-rays more nearly monochromatic. A list of the filters used for certain common targets is given in Table 1.

TABLE 1. FILTERS FOR OBTAINING MONOCHROMATIC (K_α) X-RAYS

Target	Filter	Thickness Millimeters	Grams per Square Centimeter
Chromium	Vanadium	0.0084	0.0048
Iron	Manganese	0.0075	0.0055
Cobalt	Iron	0.008	0.007
Copper	Nickel	0.0085	0.0076
Molybdenum	Zirconium	0.037	0.024

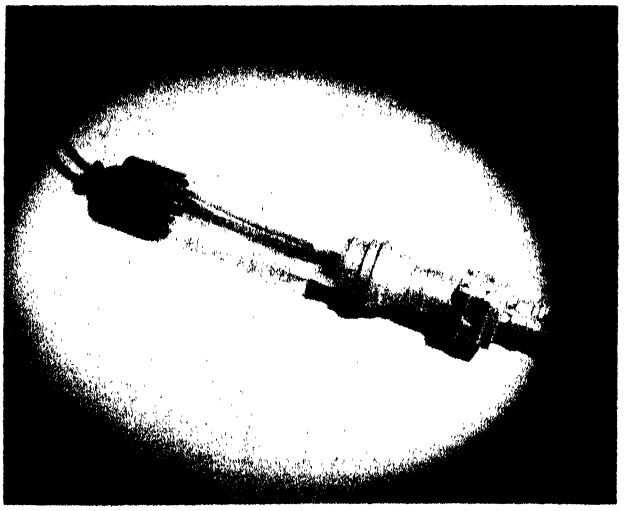
X-Ray Generating Equipment. The most common modern X-ray tube is the Coolidge or high-vacuum, heated-filament type. A diagram of such a tube is shown in Fig. VI-1. The tube is evacuated to a residual pressure of 0.01 μ or less. Electrons are emitted from the hot tungsten filament and are accelerated by a high-voltage difference toward the target. The target may be ground to a slight angle so that the X-rays, which pass through the thin exit window of beryllium foil or of a special type of glass, appear to come from a very small source. Since the target becomes very hot it is cooled by water. Some special, high-current tubes have rotating targets so that no one spot on the target becomes too hot. The targets and characteristic wavelengths of the tubes most commonly employed in diffraction work are given in Table 2.

Older types of X-ray tubes contained small amounts of gas at about 10^{-4} mm. pressure. On application of a sufficiently high voltage this gas is ionized. The electrons travel to and strike the target causing X-rays to be emitted. The relationship between voltage and current in such tubes is controlled by varying the pressure of the gas. Since the pressure is difficult to control accurately, such tubes are not used as widely at present as the heated-filament, high-vacuum type.

The X-ray generating equipment requires a high-voltage source. The equipment of several commercial manufacturers is shown in Figs. VI-2 to VI-5. The high-voltage current may be rectified by special rectifiers or, with several

TABLE 2. CHARACTERISTIC WAVELENGTH OF TARGETS USED IN X-RAY DIFFRACTION WORK

Target	$K_{\alpha 1}$ Angstroms	$K_{\alpha 2}$ Angstroms	K_{α} av. Angstroms	$K_{\beta 1}$ Angstroms	Minimum Potential Required to Excite K Lines Kilovolts
Chromium	2.28962	2.29352	2.2909	2.08479	5.98
Iron	1.93597	1.93991	1.9373	1.75654	7.10
Cobalt	1.78890	1.79279	1.7902	1.62073	7.71
Nickel	1.65783	1.66168	1.6591	1.50008	8.29
Copper	1.54050	1.54434	1.5418	1.39217	8.86
Molybdenum	0.70926	0.71354	0.7107	0.63225	20.0



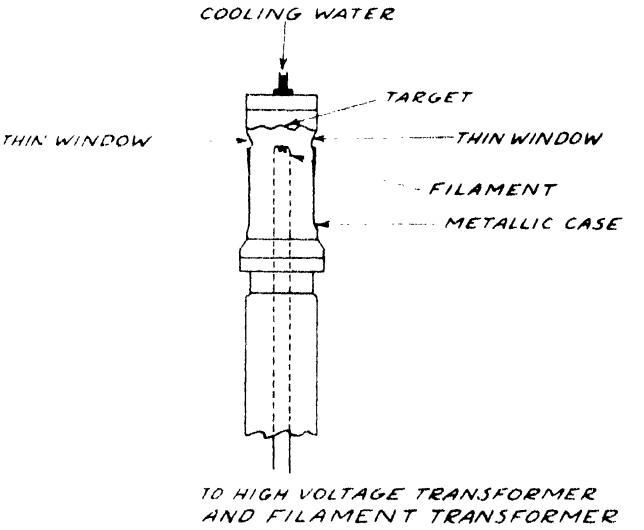


Fig. VI-1. Modern X-Ray Tube, Coolidge Type (Courtesy of Machlett Laboratories)

makes of X-ray tubes, the alternating current may be applied directly to the tube. In the latter case, X-rays will be produced only during that part of the cycle when the target is positive.

Powder Diffraction Patterns. When a beam of X-rays strikes a crystal, the planes of the crystal diffract the beam much as a grating diffracts ordinary light. The relationship between the wavelength, λ, the angle of diffraction, θ, and the distance between the planes in the crystal, d, is given by the Bragg equation:

$$n\lambda = 2d \sin \theta \qquad (4)$$

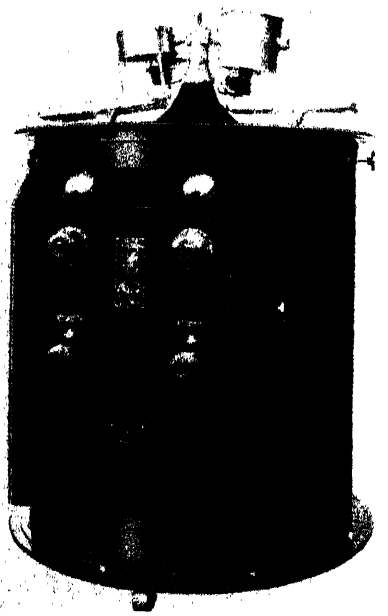


Fig. VI-2. Hayes X-Ray Diffraction Unit (Courtesy of Hayes Scientific Appliances)

Fig. VI-3. General Electric X-Ray Diffraction Equipment (Courtesy of General Electric X-Ray Corporation)

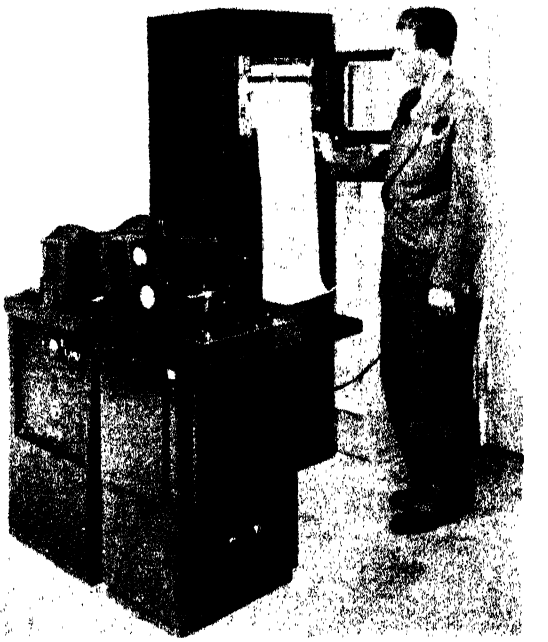


Fig. VI-4. North American Philips' X-Ray Diffraction Equipment (Courtesy North American Philips Company, Inc.)

Fig. VI-5. Picker X-Ray Diffraction Equipment (Courtesy of Picker X-Ray Corporation)

where n represents the order of the diffraction.

If the X-ray beam is monochromatic, there will be only a limited number of angles, θ, at which diffraction of the beam will occur. The actual angles are determined by the wavelength and the spacing between the various planes of the crystal. If, further, instead of using a single crystal as in the Bragg method, many very small crystals, randomly oriented, are placed in the X-ray beam, a continuous cone of diffracted rays will be produced. The cone will intercept a circular film surrounding the sample in curved lines. If the radius of the circular film is known, the angle θ can be calculated. If the wavelength of the X-rays is further known, the spacing of the planes in the crystal can be determined. This method is known as the Debye-Hull-Sherrer powder method.

As suggested above, the diffracted beams of X-rays may be recorded on a photographic film. With X-rays, the density is directly proportional to the exposure for densities up to 1 or more, and the density does not vary directly with the logarithm of the exposure until densities of 3 or more are reached. Since one is usually working at densities around 1 or below, the direct relationship between density and exposure simplifies the measurement of intensity.

The intensity of a beam of X-rays can also be measured by means of a Geiger-Müller tube or by an ionization chamber. Recently a method has been proposed[1] in which the X-rays are allowed to impinge on a fluorescent screen and the resulting light is measured by a photomultiplier tube.

Hanawalt, Rinn, and Frevel[2] have devised an indexing scheme for powder patterns of crystalline substances. They calculate the interplanar spacings corresponding to the lines produced on the film. Each substance is then classified according to the spacings producing the three most intense lines. The primary classification is on the basis of the spacing of the most intense line, the secondary classification on the basis of the next most intense line, etc. The identification of an unknown substance is then simply a matter of looking up in a file of cards that substance which has the three intense lines found on the powder diffraction picture. The American Society for Testing Materials, the American Society for X-Ray and Electron Diffraction, and, more recently, the Armour Research Foundation are cooperating in the collection, indexing, and distribution of such data on powder patterns.

It is somewhat more difficult to identify mixtures by this procedure since overlapping of the lines may produce apparently intense lines and since the second brightest line of the composite pattern may be the most intense line of the second constituent. With a little care and practice, identification of several constituents is possible. The spacing of all of the lines appearing for each substance and their relative intensities are given on each card for further help in identification. One must allow a few hundredths of an angstrom unit for error in the measured or in the recorded values of the interplanar spacing when using these index cards. Visual observation of the relative intensities is usually sufficient for identification purposes. Frevel[3] cites several examples of the use of the powder diffraction method and also discusses some of the difficulties encountered.

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LABORATORY WORK ON X-RAY POWDER DIFFRACTION

General Instructions for Operation of Hayes X-Ray Diffraction Unit

1. Check to be sure that the main switch to the instrument (upper, left-hand dial), the circuit-breaker switch (upper center part of panel) and the tube current regulator (upper right-hand dial) are all OFF.
2. Set the voltage controls at the selected voltage. The copper target tube is the tube most frequently employed. (Thirty kilovolts is recommended for usual work with the copper target tube. This is below the maximum rated value and thus increases the tube life.) The lower left-hand dial sets the tens and the kilovoltage.
3. Place the loaded powder camera (see below) on the nipple extending from the X-ray tube. Plug the motor line cord into the 110 volt receptacle on the side of the unit. Remove the lead foil behind the nipple and carefully insert the proper filter for the X-ray target employed (see Table 2).
4. Turn on the cooling water to the tube as fast as the water will run.
5. Turn on the power to the unit at the main switch box on the wall.
6. Turn on the upper left-hand main switch of the instrument. The camera motor should now operate.

7. Turn on the circuit-breaker switch on the upper center of the instrument panel. The sensitivity adjustment just below the switch may be set to 2 or 3.

8. Gradually increase the tube current by turning the upper right-hand dial until the milliammeter shows the proper current. A current of not more than 10 to 15 milliamperes is recommended for use with the copper target tube in order to increase the tube life. The apparatus will run with only occasional attention to see that the tube current is correct.

9. When shutting the apparatus off, proceed in the reverse manner to turning it on; that is, shut off the tube current, turn off the circuit breaker switch, turn off the instrument power, the water, and the main power switch.

Identification of Substances by Powder Diffraction Method

1. A very small sample of a crystalline material will be furnished. The sample must be very finely powdered (finer than 200 mesh) if it is not already so.

2. Prepare a small diameter, thin-walled melting point tube (diameter 0.7 mm. or less) and fill with the powdered sample. Place the tube in the chuck at the center of the powder camera and affix it in place with a drop of wax. Line the sample tube up so that it rotates without wobbling. Alternatively, the sample may be coated on the outside of a very fine glass rod using collodion or some noncrystalline material to stick it on.

3. Place a pinhole in the end of the collimating tube. The pinhole reading 0.025 inch on the small end is the size usually employed.

4. Take the camera into the darkroom and load it with a piece of X-ray film. An 8-inch film will cover one half the circumference of the camera. It should be roughly centered around the beam trap. The black paper covering the film is left on. The grooves in the film retaining rings are wide enough to hold film and two thicknesses of paper. Be sure the beam trap is in the raised position and turned so that it will trap the main X-ray beam.

5. Place the cover on the camera and put the camera in place on the X-ray unit. Two cameras can be used at one time. An exposure of about $2\frac{1}{2}$ to $3\frac{1}{2}$ hours will be necessary with Agfa or Eastman Non-Screen or similar film, the recommended operating conditions, and the usual type of sample. Before the end of each exposure, pull the beam trap down for a second. This will produce a center spot where the undiffracted beam hits the film directly.

6. Remove the film in the darkroom. Develop for 4 minutes in X-ray developer and fix for twice the time required for the film to clear. Wash thoroughly and dry.

7. Measure the distance between lines on the film using the film measuring device. The radius of the Hayes powder camera is 7 cm. Calculate the interplanar spacings creating the observed lines. For precise measurements of the camera radius and for compensating for film shrinkage during development, a pattern of sodium chloride may be taken. The main spacings in the sodium chloride pattern are 2.814, 1.99, 1.63, and 1.260 Å. Refer to the tables of compounds in the library to identify the unknown. Turn in all calculations, the film, and the identification of the unknown to the instructor.

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CHAPTER VII

RADIOACTIVITY

More than fifty years have passed since the discovery of radioactivity by Henri Becquerel in 1896. Until the advent of the cyclotron and more recently the chain-reacting pile, most of the work with radioactivity was with the heavy, naturally-occurring radioactive elements. It is now possible to obtain radioactive isotopes of nearly all of the elements and to obtain many of these in large quantities with extremely high activity. The availability of radioactive isotopes has given great impetus to their use.

Nature of Radioactive Disintegration

There are several different particles found in the disintegration of different elements; and, since the properties of these particles are quite different, they present different problems of measurement. The heavy, naturally occurring radioactive elements - such as thorium, uranium, and the like - emit, among other products, doubly ionized helium particles known as alpha particles. The alpha particles have only a slight penetrating power, being stopped by thin sheets of solid materials and penetrating only a few centimeters of air. Their energies are generally quite high, however, ranging up to over 10 million electron volts (mev.). The ionizing power of an alpha particle is high; that is, on passing through material a large number of ionized atoms are produced along the path traversed by the alpha particle.

A large number of radioactive elements disintegrate with the production of beta rays. Beta rays consist of either electrons or positrons which have been ejected from the nucleus of the disintegrating atom. The beta rays from radioactive elements vary greatly in their energies, ranging from a few thousand electron volts up to several million electron volts. The highest energy beta rays move at high velocities approaching that of light. The penetrating power of an electron or positron is much greater than that of an alpha particle with the same energy, but the ionizing power is much less. The penetrating power, or range, of a beta ray depends on its energy, which is usually expressed as the grams per square centimeter of aluminum or the number of centimeters of air required for complete absorption of the beta ray. For beta rays with energies of about 0.025 mev., the range is 0.00005 g. per cm.^{2} of aluminum, or 0.04 cm. of air. At 0.20 mev., the range is 0.045 g. per cm^2. of aluminum, or 37.5 cm. of air; and at 2.1 mev., the ranges are 1.03 g. per cm.^{2}, or 860 cm. The measuring devices employed for beta rays depend largely upon the energy of the rays.

A long-lived positron-emitting nucleus may decay by capturing one of its own orbital K electrons. Such a process is known as K-capture. The resulting ion with a vacant K orbital would then emit X-rays characteristic of that element.

Gamma rays, high-energy photons, are emitted by the excited nuclei of atoms. When the nucleus falls from the excited to the ground state, the additional energy is given off as gamma rays. Since only definite, discrete energy levels are possible, the gamma rays emitted have definite energies. The emission of gamma rays from the nucleus is, in many respects, similar to the emission of photons from electronically excited atoms, as in the production of emission spectra. The energies of gamma rays may range from a few thousand to several million electron volts. The penetrating power of the gamma ray is much greater than that of either the alpha or beta particle, but the ionizing power is less.

Gamma rays lose energy in passage through matter in three ways: By the photoelectric effect, by the Compton effect, and by pair production. The photoelectric effect is important for heavy absorbing elements and for low gamma-ray energies. It consists of a gamma ray striking an electron bound in an atom and transferring its energy completely to the electron, thus knocking it out of the atom. The Compton effect consists of a gamma ray colliding with an electron and transferring part of its energy to the electron. The electron is knocked out of the atom and a new photon of lower energy proceeds from the collision in an altered direction. The Compton effect is important for light elements with gamma rays possessing energies less than 3 mev. Pair production of a positron and an electron results when a high-energy gamma ray is annihilated following a collision with a heavy atom. Such a process is important with heavy elements and gamma rays of high energy.

Occasionally a gamma ray will give up its energy to one of the orbital electrons of the atom producing the ray. The electron is knocked out of the atom. If the electron comes from the K shell, it is known as a K internal-conversion electron, if from the L shell, an L internal-conversion electron, etc. Occasionally the gamma rays may be almost entirely converted in such a manner.

The disintegration of a radioactive element follows a probability function:

$$N = N_0 e^{-\lambda t} \quad (1)$$

where N = number of particles remaining at time t;
t = time;
N_0 = number of particles at zero time;
λ = radioactive decay constant.

When $N = 1/2\ N_0$, half of the material has decayed. This time, t 1/2, the half-life of the radioactive element, is generally used in describing radioactive elements.

$$t_{\frac{1}{2}} = \frac{0.693}{\lambda} \text{ (seconds)} \quad (2)$$

An accurate knowledge of λ is essential when working with short-lived radioisotopes in order to correct for the decay while the experiment is in progress.

Several terms are used in describing the activity of a substance. The Curie was originally defined as the amount of radon in equilibrium with 1g. of radium. There are 3.7×10^{10} disintegrating atoms per second in one Curie. It has become common practice to express the activity of other substances in Curies or millicuries, taking as 1 Curie that amount of radioelement which shows 3.7×10^{10} atoms disintegrating per second. This unit is not, however, entirely satisfactory for substances other than radium or radon. The Rutherford, abbreviated rd, has been suggested as a unit and is the amount disintegrating at the rate of 10^6 disintegrations per second.

To indicate the ionizing power of a substance, the Roentgen or r unit is sometimes used. An r unit is the amount of radiation that will, on passing through pure air under standard conditions, produce one electrostatic unit of ions, of one sign, per cubic centimeter. This unit is used to measure dosage due to gamma and other rays.

Measurement of Radioactivity

Radiation from radioactive elements can be detected and measured in many ways. The best method to employ in any specific case depends on the type of radiation and the energy of the radiation.

Alpha or beta particles may cause visible light to be emitted when they strike such substances as barium platinocyanide, calcium tungstate, or zinc sulfide. The intensity of the light emitted might be measured with photoemissive cells, or the individual disintegrations may be counted if they are not too numerous.

Any ionizing particle will cause activation and, on development, darkening of a photographic plate. This blackening can be used to measure the radiation, but better methods are available. The photographic plate is useful, however, in studies of the distribution of radioactive material in a thin section of a substance. A slice of tissue, for example, when placed on a plate, would cause blackening at the places where a radioactive tracer had been concentrated and thus would indicate the distribution of the tracer. Such a picture is known as a radiogram.[1]

One of the earliest devices used to measure the intensity of radiation was the electroscope. The rate of discharge of an electroscope depends on the ionization of the air molecules inside the chamber. The Lauritsen electroscope[2] consists of a conducting post and a very fine quartz fiber, rendered conducting by a thin deposit of a noble metal, connected together in such a manner that they can be electrically charged and then isolated from the rest of the system. When charged, the quartz fiber will fly away from the post due to the repulsion of like charges. The equilibrium position is determined by the repulsive force due to the charge and the restoring force due to the elasticity of the fiber. The position of the fiber is measured by observation with a microscope. The amount of ionization, and thus the activity of a radioactive sample, is determined by measuring the rate of movement of the fiber over a calibrated scale as the charge leaks off the device.

The electroscope is a very sensitive measuring device and must be carefully insulated from the surroundings. It must be carefully protected from moisture, from drafts and temperature inequalities, and from sudden jars or movements. The background leakage must be carefully measured and checked from time to time. The time required for measurement of a weak sample may be very long, a matter of perhaps several hours. However, the samples may be placed inside the electroscope chamber, if necessary; and then, since there are no windows which the radiation must traverse, very low energy radiation can be measured. A modified electroscope for measuring C^{14}, H^3, and similar important isotopes with low energy beta radiation is described by Henriques.[3]

1. See Yagoda, H., Ind. Eng. Chem., Anal. Ed., 15, 135 (1943).

2. Lauritsen, C. C. and Lauritsen, T., Rev. Sci. Instruments, 8, 438 (1937).

3. Henriques, F. C., et. al., Ind. Eng. Chem., Anal. Ed., 18, 349 (1946); ibid., 18, 415 (1946).

The Wilson Cloud Chamber and various beta-ray and mass spectrometers are also used to measure radiation.

The Geiger-Mueller counter tube (called, simply, a G-M tube) is the most widely used measuring device for radioactivity at the present time. It consists of a large round outer electrode with a wire stretched in the center as the second electrode, Fig. VII-1A, 1B, and 1C. The wire is maintained at a high positive potential (from 500 to 2500 volts) with respect to the outer electrode. The two electrodes are usually enclosed in a glass envelope which contains some easily ionized gas such as hydrogen or argon. About 10% of some organic vapor, such as methyl alcohol, may also be added. The total pressure of the gas may vary from 10 cm. of mercury up to 1 atmosphere. The tube may have a thin window of mica at one end to allow particles to enter the tube readily. Several examples of commercial G-M tubes are shown in Figs. VII-2 to VII-3.

When an ionizing particle enters a G-M tube, the ions produced are accelerated by the high voltage toward the oppositely charged electrode. Since the accelerating voltage is high, each ion may reach a sufficiently high energy to cause additional ionization upon collision with the gas molecules in the tube. Each original particle entering the tube may thus give rise to a whole "avalanche" of ions. When these ions reach the electrodes a pulse of current is produced. This pulse can be registered and counted by suitable electronic devices. Unless the ionization is stopped or "quenched" somehow, the tube would not cease conducting. The organic vapor introduced with the gas filling will quench the discharge in a very small fraction of a second (approximately 1 microsecond), or the discharge may be stopped by momentarily decreasing the voltage applied to the tube so that no more ions are produced. A circuit for quenching the discharge is described by Neher and Pickering.[4]

The performance of a G-M tube can be checked by placing some standard radioactive source near the tube and recording the number of counts per unit of time as the voltage applied to the tube is increased. A typical performance curve is shown in Fig. VII-4. At V_1, the threshold voltage, the tube begins to count particles entering it. From V_2 to V_3 there is a plateau region over which there is only a slight dependence of count-

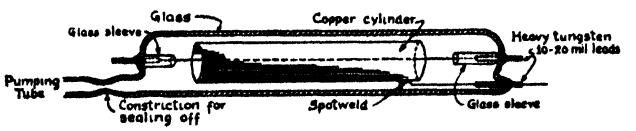

Fig. VII-1A. Typical Geiger-Muller glass envelope counter

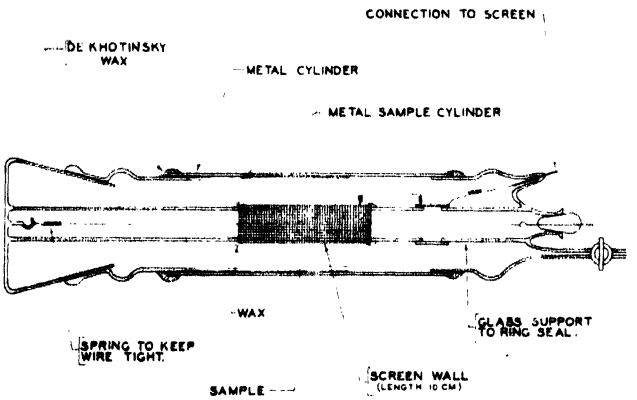

Fig. VII-1C. Diagram of a typical screen wall counter in which the solid sample is introduced directly into the counter tube (Courtesy of Anal. Chem., 19, 1947)

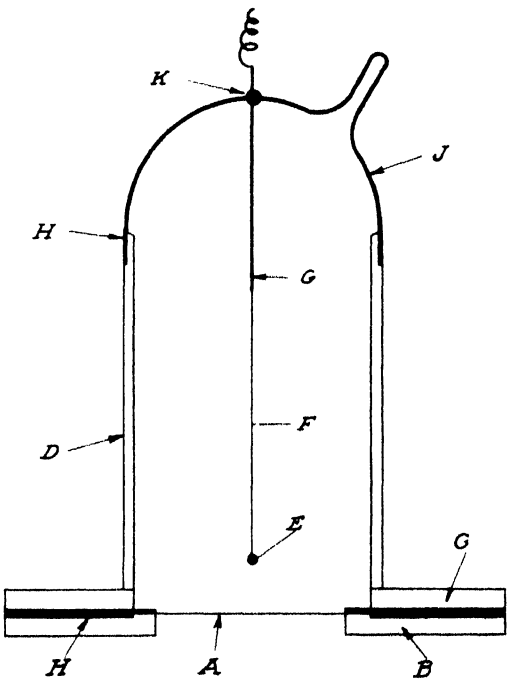

Fig. VII-1B. Bell-type pressure=seal mica window counter, helium-filled

A, Mica Wihdow (2mg. per sq. cm.) coated with colloidal graphite. B, Brass guard ring. C, copper cupport ring. D, Copper cylinder. E, Glass bead. F, 7-mil tungsten wire. G, 20-mil tungsten wire. H, Picein wax seal. J, Pyrex tube. K, Tungsten to glass seal

4. Neher, H. V. and Pickering, W. H., Phys. Rev., 53, 316 (1938).

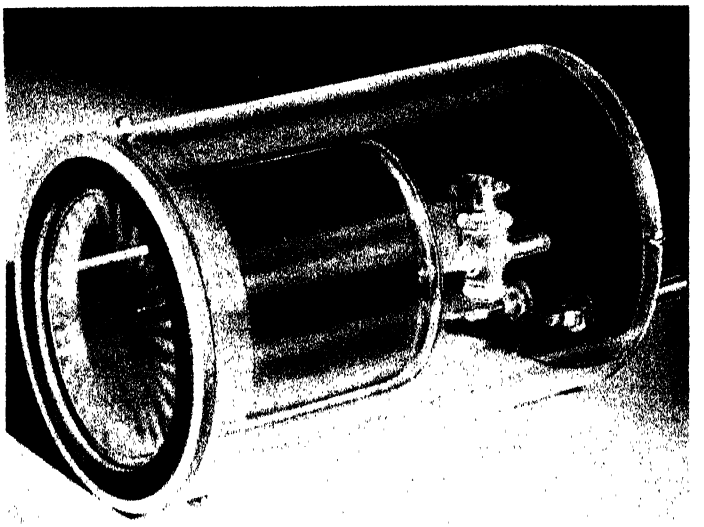

Fig. VII-2A. Cyclotron Specialties Co. End Window Geiger Counter Tube (Courtesy of Cyclotron Specialties Co.)

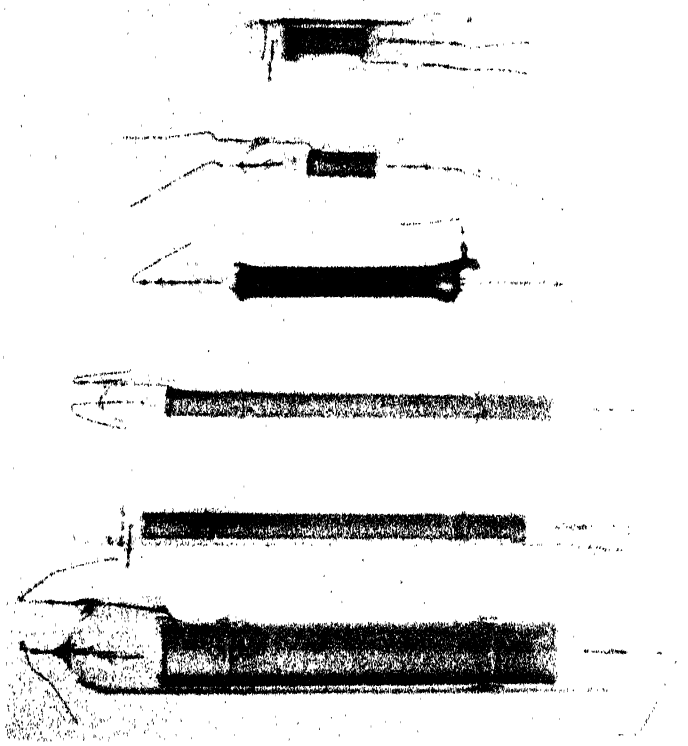

Fig. VII-2B. Geiger-Muller counters. (Courtesy of Herbach and Rademan, Inc.)

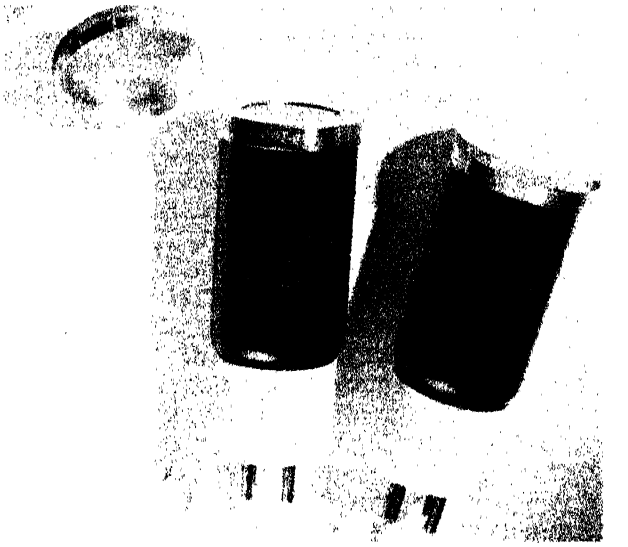

Fig. VII-2C. Tracerlab's End Window Geiger Counter Tube (Courtesy of Tracerlab, Inc.)

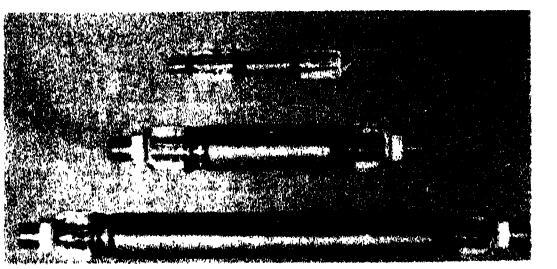

Fig. VII-2D. Amperex Side-Window Geiger Counter for Gamma rays (Courtesy of Amperex Electronic Corporation)

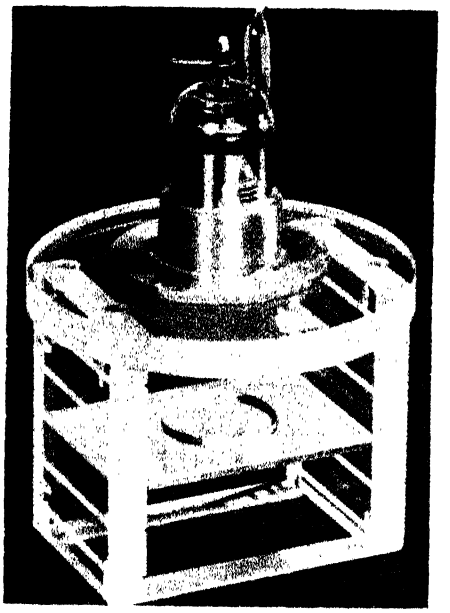

Fig. VII-3. A pressure seal mica window counter and mount. Mount has reproducible geometries of 35, 8, 3 1/2, 1 1/2, and 0.9% (Courtesy of Radiation Counter Laboratories)

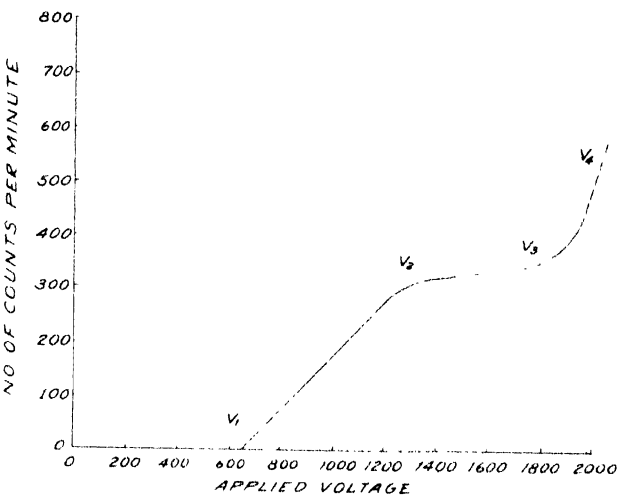

Fig. VII-4. Performance of a G-M Tube

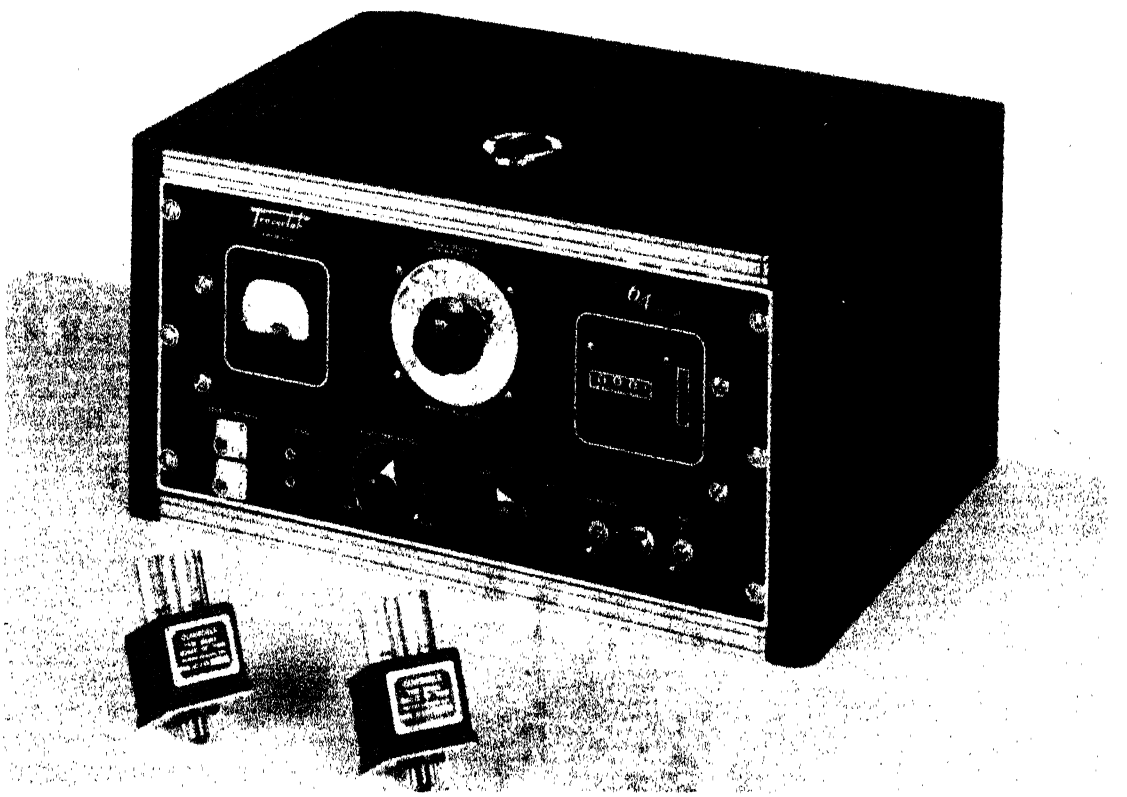

Fig. VII-5. Tracerlab's Scale-of-64 Counting Device (Courtesy of Tracerlab, Inc.)

ing rate upon the applied voltage. Beyond V_4 the tube may show a continuous discharge. A good tube will have a long plateau (several hundred volts) with little or no slope, so that, if the tube is used in this region, changes in the applied voltage have little effect on the performance.

Besides the G-M tube itself, a counting circuit and a high voltage supply are needed. These may be combined into one unit. Several commercial models are available. Some are shown in Figs. VII-5 to VII-7. The scaling circuits usually are arranged so that the mechanical recorder registers only every 2^n particle, where n may vary up to 7 or more. Neon lights permit interpolations below this number. Such circuits allow the relatively sluggish mechanical recorder to function slower than would be necessary if every single particle were to be registered by the recorder. This permits faster counting rates without loss by the counter. The recent commercial scaling circuits have resolving times exceeding 5 microseconds so that the losses due to the scaling circuit are less than 0.8% at 100,000 counts per minute. At higher counting rates, the losses become significant and calibration curves would have to be constructed by preparing a series of dilutions from a strong radioactive source.

Errors in Measurement of Radioactivity

Several factors must be considered when one attempts to determine accurately the amount of radioactive material by measuring the activity. One factor is the error caused by the counter not being perfectly efficient. This is due to several conditions; The counter may not have recovered from a previous count, the particle to be detected may not produce an ion in the sensitive volume of the counter, and various regions of the counter are more sensitive than other regions. Another factor is that the particle may never reach the counter; it may be absorbed in the walls of the counter.

The standard deviation, D - that is, the deviation to be expected of the observed number of counts from the true number, is given by the equation:

$$D = \sqrt{N} \qquad (3)$$

where D = standard deviation;
N = total number of counts.

The most probable error is defined as 0.6745 D; therefore

$$E = 0.67\sqrt{N} \qquad (4)$$

where E = probable error;
and N = number of counts.

A counter always shows some background counts due to cosmic radiation, natural radioactive substances, and other causes. It is very difficult to measure accurately a sample when the counting rate is just a little above the background rate.

Since the deviation, D, of a sum or difference of a set of counts with deviations D_1 and D_2 respectively is given by the equations:

$$D = (D_1^2 + D_2^2)^{1/2} \qquad (5)$$

$$D = (N - N_b)^{1/2} \qquad (6)$$

where D = standard deviation;
N = counts of sample plus background;
N_b = counts of background alone.

The probable error is given by equation (4) above.

If the background should be 10 counts per minute and the sample plus background should be 20 counts per minute, and if the counting should be continued for 100 minutes, the standard deviation would be

$$D = (2000 + 1000)^{1/2}$$

$$= 55$$

The probable error would be 0.67 x 55 = 37 counts. Out of the one thousand counts difference recorded in the 100 minutes, the probable error is 37 counts or 3.7%. If there were no background the probable error would be only 2.1%. It is important to keep the background as low as possible. Long counting times are necessary with dilute samples.

Weak radiation may be absorbed by the material through which it must pass to free itself from the sample. This is known as self-absorption. Libby[5] discusses this type of error in detail. Thin, uniform layers of sample are usually employed to minimize the error.

Measurement of Beta-Ray Activity

Since the majority of the radioactive elements are beta-emitters, most of the measurements are concerned with the determination of beta particles. The energy of the beta particle determines its penetrating power. Above about 0.4 mev. the

5. Libby, W. F., Anal. Chem., 19, 2 (1947).

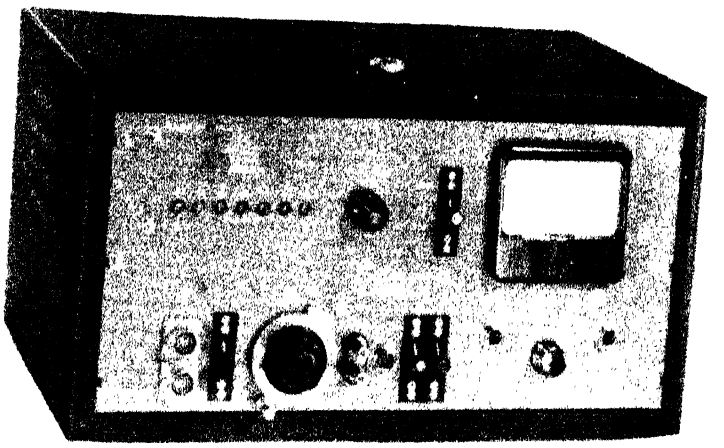

Fig. VII-6. Instrument Development Laboratories Scale of-128 Counting Device

Fig. VII-7. Victoreen Scaling Device (Courtesy Victoreen Instrument Co.)

particles have sufficient energy to penetrate the windows of most G-M tubes and measurement is not difficult. Below this energy, however, special techniques are required. Very thin window tubes may be employed, the sample may be introduced directly into the tube, or into a specially designed electrometer.[3] The introduction of radioactive material directly into a G-M tube is not generally recommended because it promotes erratic behavior and may seriously contaminate the tube with radioactive material. It is unfortunate that many of the biologically important radioisotopes, such as C^{14}, H^3, and S^{35}, have low energies and are difficult to determine.

Beta emitters with high energies can be measured in solution. Sometimes it is sufficient to use a standard size sample in a small cup placed always in the same position with respect to the

counter. The counting device described by Bale[6] has many advantages. The whole sample, or a suitable aliquot made up to 2 ml., is placed in a glass cup, the inside diameter of which is about 1 mm. greater than the outside diameter of a finger-shaped, dipping type G-M tube. The cup is mounted on a rack which brings the cup up around the counter tube to a fixed distance each time. The tube is thus surrounded by a 1 mm. thick layer of solution to the same depth at each measurement. The apparatus is quite sensitive and reproducible, but the tube may easily become contaminated with hard-to-remove radioactive material.

Solid samples may be measured after filtration on filter paper placed over a coarse-porosity, fritted glass disc. The sample must be evenly distributed on the paper and must be mounted and placed in a reproducible manner with respect to the tube. Liquid samples can be evaporated to dryness in small aluminum or other types of containers. Some elements can be electrodeposited on platinum foils.

Measurement of Gamma-Ray Activity

Due to the low ionizing power of gamma rays, a great proportion will pass through a tube designed for counting beta particles without producing any effect. The sensitivity of the counter tubes must be increased by using longer chambers and by filling the chambers with heavy gases under high pressures. In other respects, the measurements are similar to those for beta particles. If it is desired to measure gamma radiation exclusively, a shield may be inserted between the sample and the counter. The shield should be of sufficient thickness to absorb all beta particles.

Measurement of Alpha Particles

Because of the low penetrating power of alpha particles, self-absorption is quite important. It is difficult to prepare standards and unknowns in reproducible form and such that measured activity is proportional to true activity.

Any of the usual types of apparatus can be used to measure alpha particles. The ionization chamber or electroscope is preferable, however, because a single alpha particle produces a large amount of ionization within the electroscope, but would produce only one count in a G-M tube. Alpha particle activity can be measured in the presence of considerable beta activity by first measuring the total activity, then interposing a filter to absorb the alpha particles, and measuring the beta activity.

6. Bale, W. F., Haven, F. L. and LeFevre, M. L., Rev. Sci. Instruments, 10, 193 (1939).

Measurement of Neutron Activity

Neutron activity may be measured by utilizing the nuclear reaction between a boron atom and a neutron to yield two alpha particles and tritium. The reaction is quite efficient and the ionization due to the secondary alpha particles is readily measured. G-M counters for this type of work simply contain 12 to 40 cm. pressure of very pure boron trifluoride gas.

Sources of Radioactive Isotopes

The naturally occurring radioactive isotopes are generally separated from radiothorium or from the spent radon tubes used in radium therapy. The isotopes of lead, RaD (16 yr.) and ThB (10.0 hrs.), and the isotopes of bismuth, RaE (4.85 days) and ThC (60.5 min.), were the radioisotopes generally employed.

Artificially produced radioisotopes of practically all of the elements are now available, either from the chain-reacting piles or from bombardments carried out with cyclotrons. The procedure for obtaining isotopes through the Atomic Energy Commission is described in the literature.[7] Lists of the radioisotopes are given by Seaborg[8] and are found elsewhere in the literature.[9]

Applications of Radioisotopes

Since the radioactive isotopes are chemically identical to the stable isotopes they may be used to "tag" a compound. The "tagged" compound may then be followed through any analytical scheme by using a method of detecting the radioactivity. The compounds can be followed through a biological system also. It is essential, however, that the radioisotope chosen shall have a sufficiently long half-life so that reasonable amounts will be left after the process is complete. It is also necessary that a compound be "tagged" with an atom which is not readily exchangeable with similar atoms in other compounds under normal conditions. For example, radioactive H^3 could not be used to trace an acid if placed on the carboxyl group where it is readily exchanged by ionization.

In ordinary analytical work, radioisotopes

7. See Science, 103, 697 (June 14, 1946).

8. Seaborg, G. T., Chem. Reviews, 27, 199 (1940).

9. Cork, J. M., "Radioactivity and Nuclear Physics," D. Van Nostrand Co., Inc., New York, 1947, pp. 273 ff.

Hodgman (Ed.), "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, 1943, pp. 277 ff.

Lange (Ed.), "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, 1944, pp. 87 ff.

have been used to study errors of adsorption and occlusion. Hönigschmid studied the adsorption of radium on silver chloride. The precipitation of silver chloride is of fundamental importance in atomic weight determinations. If silver chloride contains excess silver nitrate, it darkens on heating; but, if it should contain radium nitrate, it would appear to be normal; however the precipitate would be radioactive. Hönigschmid's experiments proved that the silver chloride contained not more than 50 micrograms of adsorbed radium nitrate per 5 g. sample, which is quite satisfactory, and there is reason to suppose that other bivalent metals would behave similarly. Related experiments have been devised with other radioisotopes to study the amount of adsorption and methods of preventing adsorption on other precipitates.

Radioisotopes are useful in determining the solubility of very slightly soluble materials. It is necessary first to establish the ratio between radioactivity (expressed in any convenient manner - for example, counts per minute) and weight of isotope plus carrier present. This is usually established by evaporating an aliquot to dryness, weighing it, and measuring the radioactivity. The compound to be studied is synthesized using the radioisotope, and a saturated solution of the compound is prepared. A measured volume of the saturated solution is evaporated to dryness, and the radioactivity of the residue determined. From the previously established relationship between weight and radioactivity, the amount of the compound present can be calculated. This procedure has the advantage over other methods that it is not affected by the presence of other substances, especially common-ions. Thus the solubility of lead chromate, for example, could be determined in the presence of excess chromate ions using a radioisotope of lead.

The efficiency of analytical processes can be determined by adding a known amount of radioisotope to the sample before analysis is begun. After the final determination of the element in question, the radioactivity of the precipitate is determined and compared to the activity added at the start.

A classical example of the use of radioisotopes in studying the difficulties in an analytical process is that of Erbacher and Philipp.[10] They used radioactive gold in a process recommended for the separation of gold, platinum, and iridium. Known amounts of all three metals were precipitated with sodium formate, the gold and platinum dissolved with aqua regia, leaving behind the iridium, the filtrate treated with alkaline hydrogen peroxide to precipitate the gold, and the platinum finally precipitated with sodium formate in the filtrate from the gold separation. The gravimetric results showed that apparently a small amount of iridium and platinum remained unprecipitated, while the gold precipitate was too heavy. This would seem to indicate that the peroxide precipitated not only all of the gold but also a little platinum. Actually, the studies with radioactive isotopes showed that some gold, and not platinum, remained with the iridium after treatment with aqua regia, and that the gold was never completely precipitated by alkaline peroxide even though the precipitate weighed too much. Thus the procedure was not satisfactory unless carried out under carefully controlled conditions.

Langer[11] has described a titration procedure using radioisotopes. Radioactive phosphorus was converted to a soluble phosphate and added to a disodium hydrogen phosphate standard solution. This solution was used to titrate several substances such as Ba^{++}, Pb^{++}, Th^{++++}, Mg^{++}, and UO_2^{++}. After each addition of phosphate a sample of the clear, filtered solution was sucked up around a G-M tube and the activity determined. The activity remains essentially constant until the equivalence point is reached, at which point it rises rapidly with additions of reagent. From the intersections of the activity curves, the end point is accurately determined.

One of the most useful analytical techniques employing either radioactive or stable "heavy" isotopes is the isotope dilution procedure. This procedure is described by Paneth.[12]

Let P be a nonradioactive compound and P* be the same compound "tagged" with a radioactive element. The radioactivity of this "tagged" compound is represented by (act./mg.)P*. Let PP* represent the chemically indistinguishable mixture of P and P*. If the amount of P in a mixture is unknown, a known amount of P* is added to the mixture and distributed evenly throughout. A small sample of the substance PP* is now isolated in pure form. The amount isolated need be only a very small fraction of the total amount present, but it must be enough to be accurately weighed (a fraction of a milligram may be sufficient). The activity of this mixture is determined and is represented by (act./mg.)PP*. If R represents the ratio of the specific activities (act./mg.)P*/(act./mg.)PP*, then

$$\text{mg.P} = \text{mg.P*}(R-1) \qquad (7)$$

10. Erbacher and Philipp, Angew. Chem., 48, 409 (1935).

11. Langer, A., J. Phys. Chem., 45, 639 (1941).

12. Paneth, F. A., "Radioelements as Indicators," McGraw-Hill Book Co., Inc., New York, 1928.

The procedure can also be used for the determination of traces of radioactive substances, P*, by adding known amounts of P. Henriques and Margnetti[13] illustrate these procedures by a quantitative determination of the three individual components in a mixture of dibenzyl-sulfide, sulfoxide, and sulfone.

Many other uses of radioactive isotopes have been devised but cannot be described here for lack of space. Some of the uses are briefly listed below:

1. To trace the distribution and storage of various elements in plants and animals.
2. To determine the interchangeability of atoms in organic or inorganic compounds, and to elucidate the mechanism of reactions.
3. To detect the existence of unstable or volatile compounds, such as the hydrides of lead and bismuth.
4. To determine the surface area of solids.
5. To determine the effectiveness of washing of precipitates and the rinsing of laboratory apparatus.
6. To determine the age of rocks and thus an estimate of the age of the earth.
7. To study the aging of precipitates.

LABORATORY DIRECTIONS FOR RADIOACTIVITY

General Directions for Operation of the Scaling Circuit

1. Connect the mechanical register, the timing clock (a stop watch is a satisfactory substitute), the quenching circuit (if the G-M tube is not self-quenching), and the G-M tube to the scaling circuit in their proper places. The positive high-voltage lead is connected to the anode of the G-M tube.
2. Be sure that all switches are in the OFF position. Then plug the cord from the scaling circuit into a 110 volt, 60 cycle main.
3. Turn the master switch to the ON position.
4. Turn the high-voltage control(s) to the most counterclockwise position. This is to assure that the high voltage will be below the continuous discharge point of the G-M tube.
5. After the scaling circuit has warmed up for at least 30 seconds, the high-voltage switch is turned ON. If this interval of time is not observed, the G-M tube may be damaged by a surge of high voltage before the regulator tubes assume control.
6. When indicated by the high-voltage meter, slowly increase the high voltage by turning the control(s) clockwise to the operating voltage of the G-M tube. If the operating plateau is not known for a particular G-M tube, it should be determined as described under laboratory directions.
7. Extinguish the interpolation lights by momentarily depressing the reset switch. Reset the mechanical register and the timing clock. A count may now be taken.
8. Insert the sample in the desired geometric position in relation to the G-M tube. For a background count simply remove any radioactive material from the vicinity of the counter.
9. Turn the stop-count switch to COUNT. If a stop watch is used, depress the stem simultaneously.
10. After counting the desired length of time, throw the stop-count switch to STOP, and if a stop watch is being used, depress the stem simultaneously. Multiply the numbers on the mechanical register by the value of the particular scaling circuit used, that is, scale of 32, 64, or 128, and add the interpolation. The interpolation is the sum of the numbers above the neon lights that are glowing.

Note: If a non-self-quenching G-M tube is employed, an external quenching circuit must be used between the G-M tube and the scaling circuit. The bias control on the quenching circuit should be adjusted according to the instructions accompanying the particular instrument.

Preparation of a Series of Radioactive samples.

Student samples, which are both satisfactory and safe to handle, may be prepared from a solution of a uranyl salt. Dissolve 1.25 g. of uranyl acetate in 50 ml. of distilled water in a volumetric flask. Mix thoroughly, then pipet suitable aliquots into small aluminum sample pans which have been lightly greased around the rims. Satisfactory weights of uranyl acetate constitute a series: 10, 15, 20, 25, 30, 35, 40, 45, and 50 mg. of salt per sample. Remove the solvent by evaporation with an overhead heat lamp. When dry, cover the sample with a thin sheet of aluminum foil to remove all the alpha particles. The counting rate per minute for each sample must be found empirically by the instructor. Usually the heaviest sample will have a counting rate exceeding 1000 counts per minute.

Suggested Laboratory Experiments

The type of radioactivity measurements and

13. Henriques, F. C. and Margnetti, C., Ind. Eng. Chem., Anal. Ed., 18, 476 (1946).

the scope of the work must depend upon the type of equipment available, the radioactive source, and the student time allotted to the experiment. Experiments involving the determination of the counting rate plateau and the statistical error in counting will be described. These experiments may be executed with the minimum of equipment. Use of a dip type counter will also be described.

Determination of the Counting Rate Plateau

1. Assemble the equipment and warm up the scaling circuit as described in the general directions 1-5.
2. Insert a radioactive sample under the counter tube, preferably a sample yielding at least 1000 counts per minute.
3. Extinguish the interpolation lights; reset the mechanical register and timing clock. Turn the stop-count switch to COUNT.
4. Slowly increase the high voltage by turning the control clockwise until the threshold voltage is exceeded and counts begin to register on the scaling circuit.
5. Proceed from the threshold value and determine the counting rate as a function of the high voltage. Immediately beyond the threshold voltage a rapid rise in counting rate will be noticed until the Geiger-region is reached. DO NOT INCREASE the high voltage beyond the plateau portion, the termination of which will be noted by a second rapid increase in counting rate as the high voltage is continually raised. If the high voltage is increased beyond this point, a continuous discharge will result and the G-M tube will be damaged.
6. Plot the counting rate per minute as ordinate against the voltage as abscissa.

Probable Error in Counting

1. Prepare the scaling circuit and counting tube as described under general directions. Obtain a series of radioactive samples from the instructor.
2. The object of this experiment is to count each of the samples within the statistical accuracy requested by the instructor. First, insert the samples successively in the desired geometric position and determine the counting rate roughly for a 1 minute interval. Determine the background similarly.
3. From the approximate counting rate and background, calculate the length of time both the background and the sample must be counted to attain the statistical accuracy desired. Use the formulas given on page 98.
4. Commence counting each of the samples for the length of time that has been calculated. If the uranium series of samples were used, no correction is necessary for the decay. Report all results corrected for background, including the counting time.

Laboratory Directions for Dip Type Counter.[14,15]

If equipment is available for work on solutions using a dip type G-M tube, examination of solutions of UO_2SO_4, $K^{42}Cl$, $Na^{24}Cl$, $Na_2HP^{32}O_4$, and NaI^{131} may be carried out. A visual colorimeter may be modified to provide a convenient rack and pinion arrangement for raising and lowering the sample cup over the counting tube. Water is a suitable solvent.

The cup should be of such a size to give a clearance of 1.5 mm. Centering is not too stringent; for an error of 1% the sample cup must be within 0.25 mm. of its proper center. The height of the liquid in the tube is not critical as long as it at least covers the silvered portion of the counter tube. The temperature of the solution including rinse water should be held constant to 1°C.

The procedure for rinsing: Wipe the counter with a piece of absorbent tissue, rinse with distilled water, and again wipe the counter with absorbent tissue. Repeat the process once more, although one wiping, followed by rinsing and another wiping, usually removes all traces of activity.

Procedure:

1. Calibrate the counter tube with at least two solutions of known concentration and density.
2. The observed counts per minute, (c/m), and the known density, (d), of the calibrating solutions are substituted in the following equation:

$$\log (c/m) = k - (a)(d)$$

and the constants k and a evaluated.

3. Determine the counting rate and the density of the unknown solutions. Substitute the values in the above equation and calculate the salt concentration. If water solutions containing only the radioactive material are used, the density correction may be omitted and the results plotted graphically as counting rate vs. concentration of salt.

14. Solomon, A. K. and Estes, H. D., Rev. Sci. Instruments, 19, 47 (1948).

15. Barnes, R. B. and Salley, D. J., Ind. Eng. Chem., Anal. Ed., 15, 4 (1943).

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2. Hevesy, G. and Paneth, F. A., "Radioactivity," 2nd Edition, Oxford Univ. Press, London, 1938.
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4. Lewis, W. B., "Electrical Counting with Special Reference to Counting Alpha and Beta Particles," The Macmillan Co., New York, 1943.
5. Paneth, F. A., "Radio-Elements as Indicators," McGraw-Hill Book Co., Inc., New York, 1928.
6. Seaborg, G. T., Science, 105, 349 (1947).
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CHAPTER VIII

THE REFRACTOMETER AND INTERFEROMETER

When a ray of light passes obliquely from one medium into another of different density, its direction is changed on passing through the surface. This is called refraction. If the second medium is optically denser than the first, the ray will become more nearly perpendicular to the dividing surface. The angle between the ray in the first medium and the perpendicular to the dividing surface is called the angle of incidence, i, while the corresponding angle in the second medium is called the angle of refraction, r. Sine i and sine r are directly proportional to the velocities of the light in the two media. The ratio $\frac{\text{sine i}}{\text{sine r}}$ is called the index of refraction, N. If the incident ray is in the denser medium, N will be less than 1; if in the rarer, greater than 1. N is commonly taken as greater than 1, the ray passing from the optically rarer medium (usually air) to the denser.

The index of refraction for two given media varies with the temperature and the wavelength of light, and also with the pressure if we are dealing with a gas. If these factors are kept constant, the index of refraction is a characteristic constant for the particular medium and is used in identifying or determining the purity of substances and for determining the composition of homogeneous binary mixtures of known constituents.

The refractive index is theoretically referred to vacuum as the first medium, but the index referred to air differs from this by only 0.03% and, for convenience, is more commonly used. The symbol N_D^{20} means the index of refraction for the D lines of sodium measured at 20°C.

When the beam of light passes from a denser to a rarer medium, the angle r will be greater than the angle i. As angle i increases, the ratio $\frac{\text{sine i}}{\text{sine r}}$ remaining constant, the angle r must also increase and remain greater than i. If angle i is increased to the value where r becomes 90 degrees, the beam of light will no longer pass from the first medium to the second, but will travel through the first medium to the dividing surface and then pass along this surface, thus making 90° with the perpendicular to the surface (see Fig. VIII-1). If i is smaller than this particular

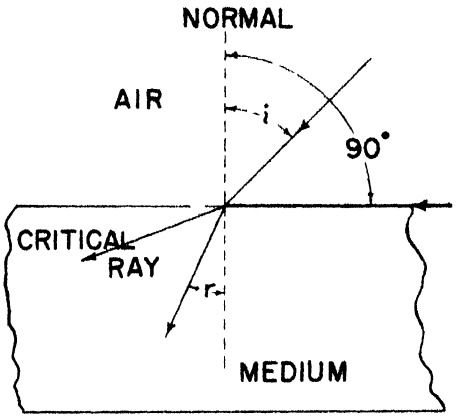


Fig. VIII-1

value, light will pass on through the second medium; if greater, all light will be reflected from the surface back into the first medium. This furnishes the basis for the reference line used in several refractometers. Total reflection can occur only when light passes from the denser to the rarer medium.

Specific refraction depends only on the nature of the substance. If we multiply it by the molecular weight, we obtain molecular refraction which is a more or less additive property of the groups or elements composing the compounds. Specific refraction is valuable in confirming the identification of a substance in this way: If the nature of it is known - aldehyde, acid, ketone, etc. - its identification can be confirmed by the relation of its specific refraction to that of the neighboring compounds. If the boiling point or melting point is known, then specific refraction helps a good deal. [1]

REFRACTOMETERS

There are three common types of refractometers, the Abbe, the immersion or dipping, and the Pulfrich instruments. The latter uses monochromatic light, requires more of the sample than the Abbe type, and is, therefore, less commonly used.

The Abbe Refractometer. The range of this instrument is 1.3000 to 1.7000, the maximum

1. Schoorl, N., Rec. Trav. Chem., 39, 594 (1920). Herz, W., Z. physik. Chem., 98, 175 (1921).

accuracy attainable being 0.0001. It reads refractive index directly, is durable, requires only a drop of sample, and gives a good approximation of partial dispersions. White light is used and, to prevent a colored, indistinct boundary between the light and dark fields due to the differences in refractive indices for light of different wavelengths, two direct vision prisms, called Amici prisms, are placed one above the other in front of the objective of the telescope. These are constructed of different varieties of glass and are so designed as not to deviate a ray of light corresponding to the sodium D line. Rays of other wavelengths are, however, deviated and, by rotating these Amici prisms, it is possible to counteract the dispersion of light at the liquid interface.

The essential parts of the instrument are shown in Fig. VIII-2 and the instrument itself in

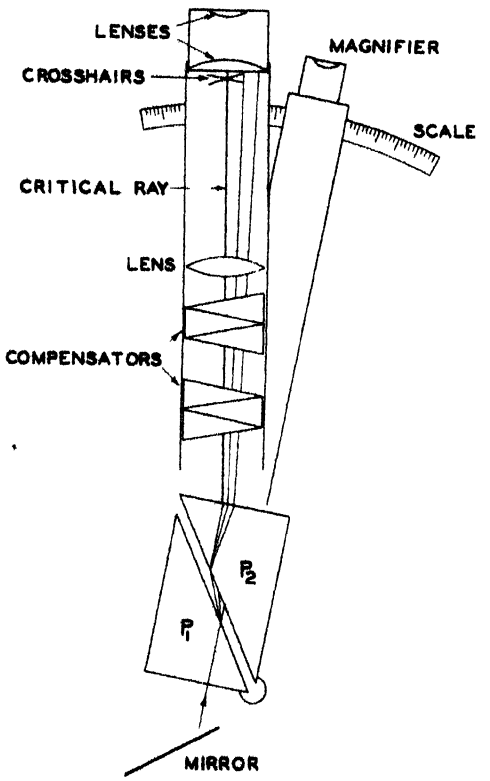
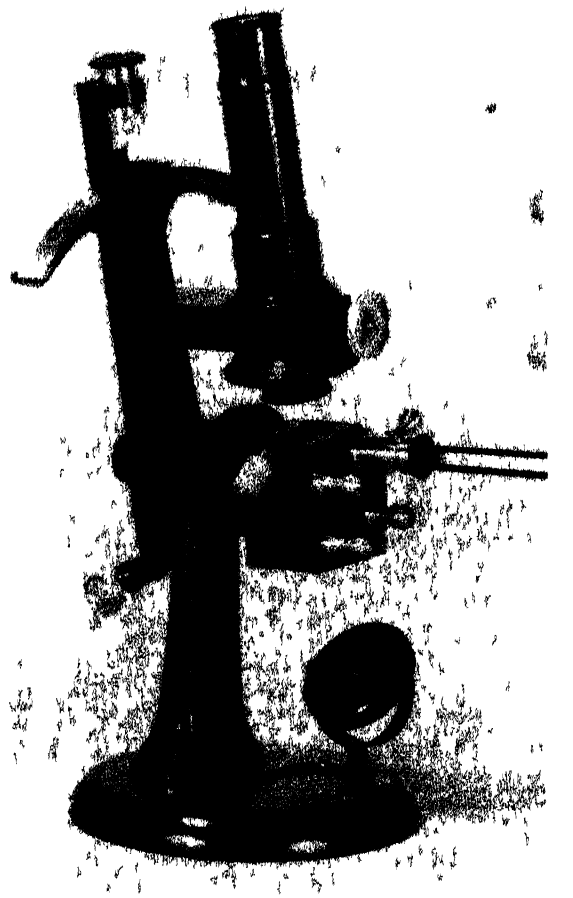


Fig. VIII-2

Fig. VIII-3. Light reflected from a mirror passes into the illuminating prism P_1, the upper surface of which is rough ground. This rough surface acts as the source of an infinite number of rays which pass through the 0.1 mm. layer of liquid in all directions. These rays then strike the surface of the polished prism P_2 and are refracted.



Bausch & Lomb

Fig. VIII-3

The critical ray forms the border between the light and dark portions of the field when viewed with the telescope which moves with the scale. The scale is provided with a reading telescope.

The temperature should be controlled within $\pm$ 0.2°C. The instrument is fitted with hollow prism casings through which water may be passed. A short thermometer is inserted into the water-jacket. The most satisfactory temperature control is obtained by using a small circulating pump to pass water from a thermostat through the prism casing.

The Immersion Refractometer. This type is the simplest to use but requires 10-15 ml. of sample. It uses white or artificial light and contains an Amici compensator as already described. The single prism is mounted rigidly in the telescope containing the compensator and eyepiece as shown in Fig. VIII-4. The scale is mounted

below the eyepiece inside the tube. The lower surface of the prism is immersed in a small beaker containing the sample with a mirror below to reflect light up through the liquid. The complete instrument in position with the water bath

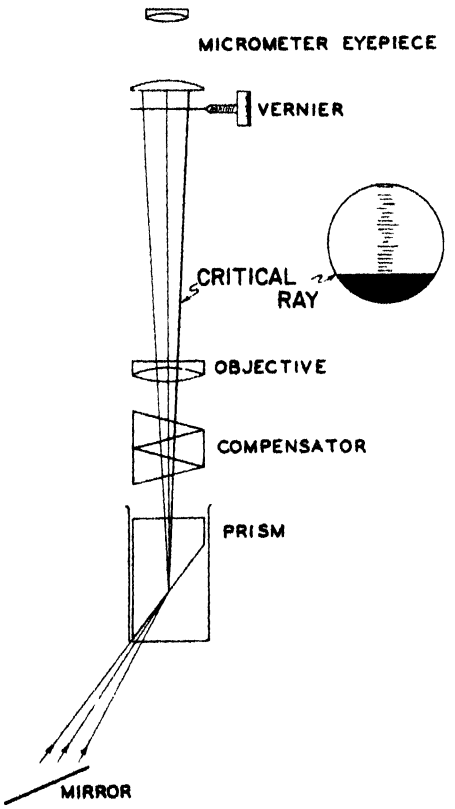
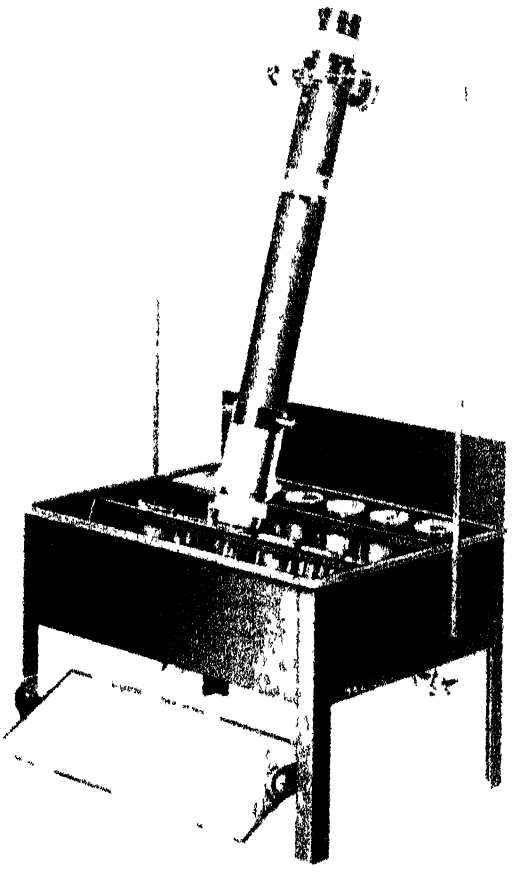


Fig. VIII-4

for maintaining a constant temperature is shown in Fig. VIII-5.

The scale, situated at the focal plane of the eyepiece, is graduated from -5 to +105. The field will be partly dark and partly light, separated by a sharp line as already explained (see Fig. VIII-1). The position of this line is read on the scale, and the tenths of a division are found by turning a micrometer screw at the top of the instrument, which slides the scale toward the border line until it covers the lower numerical scale division previously noted. The figure on the micrometer drum then shows the decimal to be added. A change of 0.01 division corresponds to $\pm$ 0.000037 in N_D. The immersion refractometer therefore gives greater precision in its readings than any other type except the interference refractometer.



Bausch & Lomb

Fig. VIII-5

Since the refractive index changes with the temperature, a standard temperature must be chosen. This, unfortunately, is 17.5° C. which is rather difficult to maintain. The solution to be tested is placed in a very small, specially designed beaker placed in a rack in a water bath illuminated through the bottom. Through the bath is passed a current of water at the proper temperature. This may be done by running tap water from a constant level tank, into the bath, at the proper rate; or, various types of constant temperature baths may be used.

The correctly adjusted refractometer should show for distilled water at various temperatures the following readings:

15°	16°	17°	17.5°	18°	19°	20°	21°
15.5	15.3	15.1	15.0	14.9	14.7	14.5	14.25
22°	23°	24°	25°				
14.0	13.75	13.5	13.25				

The temperature should not vary more than 0.1° C. because readings are reported to an estimated 0.01 scale division. In order to be of any value the reading must be converted into concentration by means of published tables, the most comprehensive of which are those by Wagner, obtainable from suppliers of the instrument. These tables apply only to 17.5° and there is no formula for converting them to other temperatures. There are, however, tables for methyl and ethyl alcohol at other temperatures. Leach and Lythgoe[2] have published complete data for 20°. The table is included in the Appendix. The table by Andrews[3] covers only the range 70-100% ethyl alcohol at 25°. In all tables, readings are only given in scale divisions. Readings may be converted into index of refraction by reference to tables furnished with the instrument.

The range of the instrument with prism 1 is 1.325 to 1.367. This covers all ordinary salt solutions and alcohols. For higher values special auxiliary prisms are furnished extending the range to 1.492. Thus the range of this refractometer is much narrower than that of the Abbe, but this gives it the advantage of greater sensitivity.

A disadvantage of refractometric analysis is the necessity for carefully regulating the temperature. An attempt has been made by Clemens[4] to avoid this, but considerable precision was necessarily sacrificed.

The refractometer measures concentration more accurately and readily than can be done by ordinary density measurements with a hydrometer. For example, assuming a sufficiently accurate temperature control, 0.02 scale division, which is about the best one can do in reading the instrument (estimating the nearest 0.01 division) corresponds to the following weight of substances per 100 ml.: methyl alcohol, 24 mg.; ethyl alcohol, 12 mg.; ammonium chloride, 4 mg.; perchloric acid, 10 mg.

If both density and refractometer readings are determined, it is possible to determine each of two components, such as methyl and ethyl alcohol, with a fair degree of accuracy if nothing else is present. It should be noted that both density and refractive index are measures of the total amount of substance in solution no matter how many different ones there may be.

Uses. The immersion refractometer is especially useful in determining the concentration of aqueous and alcoholic solutions. Wagner[5] describes precautions to be used, such as constancy of temperature, rinsing prism with water of same temperature; wiping lightly and allowing 2 minutes before reading.

Shippy and Barrows[6] showed how index of refraction could be used to determine the composition of solutions of sodium chloride and potassium chloride. A curve was constructed by plotting percentage of sodium chloride against index of refraction. A fair degree of accuracy was attained.

In physiological chemistry the refractometer is very important. In only 2 ml. of serum, it can be used to determine nonalbuminous constituents, total globulins, insoluble globulins, albumens, and total albumen, with great accuracy.[7] The action of ferments can be followed with the refractometer. The refractometer is also useful in controlling the analysis of commercial products, in identifying unknown substances, in distinguishing substances of the same boiling point and compounds of the same nature, such as halogenated hydrocarbons.

THE INTERFEROMETER

Refractometers are dependent upon the diffraction of light when passing from one substance to another. The finest measurement of refractive index, however, is based upon the interference of light. In this method there is no diffraction. The light enters and leaves the solution at right angles. The interferometer, reduced to its simplest terms, may be represented by Fig. VIII-6.[8]

Parallel light passes through two small openings, R_1 and R_2 in Fig. VIII-6. Since R_1O and R_2O are of equal length, the two beams arrive at O in phase and a bright spot results. At other points on the screen the lengths of the two beams are not the same. Thus at some point, x, the two beams differ by half a wavelength. Interference of the two beams produces a dark spot

2. Leach, A. E. and Lythgoe, H. C., J. Am. Chem. Soc., 27, 964 (1905).

3. Andrews, L. W., J. Am. Chem. Soc., 30, (1908).

4. Clemens, C. A., J. Ind. Eng. Chem., 13, 813 (1921).

5. Wagner, B., Z. angew. Chem., 33, I, 262 (1920).

6. Shippy, B. A. and Barrows, G. H., J. Am. Chem. Soc., 40, 185 (1918).

7. Hirsch, Z. angew. Chemie., 33, I, 269 (1920).

8. Adams, J. Am. Chem Soc., 37, 1181 (1915).

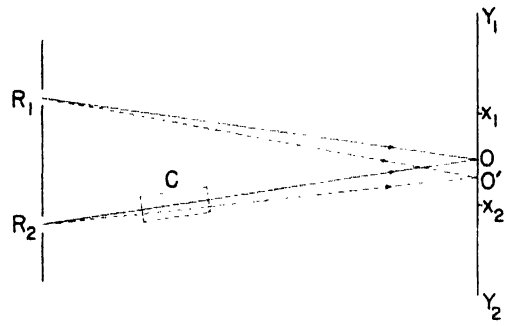


Fig. VIII-6

here. At a point a little farther along, Y, the difference is 1 wavelength and a bright spot is formed. With monochromatic light, this succession of light and dark spots (maximum and minimum) continues indefinitely. Now, if a substance of slightly greater refractive index be placed at C, the optical length, p, of the beam R_2O is increased because the velocity of light through C is decreased. The magnitude of this increase depends on the thickness of C and upon its refractive index.
Where

p = l (n - n_o)
l = thickness of C;
n = refractive index of C;
n = refractive index of medium (air).

The velocities of light in two media are proportional to their indices of refraction.

The two beams will no longer arrive in phase at O, but at some other point O', which is now optically equally distant from R_1 and R_2. The entire band system will be shifted by this amount. For light of wavelength, λ, the distance between O and O', measured in numbers of fringes, N, (each made up of dark and light band), is

$$N = p/\lambda$$

or

$$N = l\,(n-n_o)$$

If N is greater than 1, it is impossible to tell how many whole numbers of bands greater it is, since all bands are alike. This difficulty is avoided by using white light instead of monochromatic. Now the central band is the only one which is pure white. The bands on either side of this maximum of the first order are fringed with blue toward the center of the system and with red along the outer edge. This is due to the different wavelengths which go to make up white light. The next adjacent bands are even more highly fringed. After six or seven bands, the diffusion is so great that the rest of the field is again uniformly white. Thus, with substance C in the path of one of the beams, by counting the number of bands which the central band has been shifted, we may determine the value of l (n-n_o). Anyone of these terms can then be calculated if the others are known. If two plates of equal thickness were placed in the two beams, the number of bands that the central band shifts would be a means of calculating the refractive index of one of the plates, provided that the value of the other one was known. The interferometer is, however, not used primarily for measuring index of refraction but for comparing and measuring concentrations of solutions and gases.

In one type of instrument shown in Fig VIII-7, the optical length of the two beams is equalized

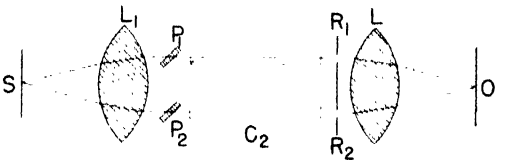


Fig. VIII-7

by means of a glass plate in the path of each beam (p_1 and p_2) at an angle of about 45° to the beam, one plate being fixed and the other attached to a lever by which it can be rotated, thus increasing or decreasing its effective thickness. The movement is measured by a micrometer screw. This is turned until the central achromatic bands of the two systems correspond, - that is, the optical path of the two beams is the same length. It is possible to match them to one-twentieth of a band, corresponding to a reading of about one scale division on the micrometer screw. This instrument was originally used for measuring changes in the composition of gases, and, using gas chambers 1 meter long, one scale division corresponds to a change in N_D of 0.000000015. It is capable, therefore, of measuring quantities of such substances as CO_2 and CH_4 present in air in amounts as low as 0.02%.

In a later type of portable gas and water interferometer, made by Zeiss, and shown in Fig. VIII-8, the light is reflected by the mirror, M, so that it passes twice through the chambers and the bands are observed at the same end as the light source. In this way it is possible to obtain the same precision with half the length. The

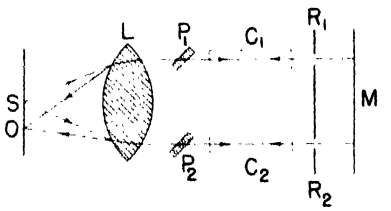


Fig. VIII-8

light is furnished by a small electric light, which is focused on a slit. The interference bands are not as brilliant as those of the other instrument but are just as plain and as easily set. The chambers can be jacketed with an air thermostat or with water, and gases as well as liquids can be used. With the latter, the cells vary from 1 to 40 mm. in length. The scale reading is proportional to the thickness of the liquid, so that the range and precision of the instrument may be varied by changing the length of the cell.

A diagram in plan and elevation of the Zeiss water interferometer is shown in Fig. VIII-9.

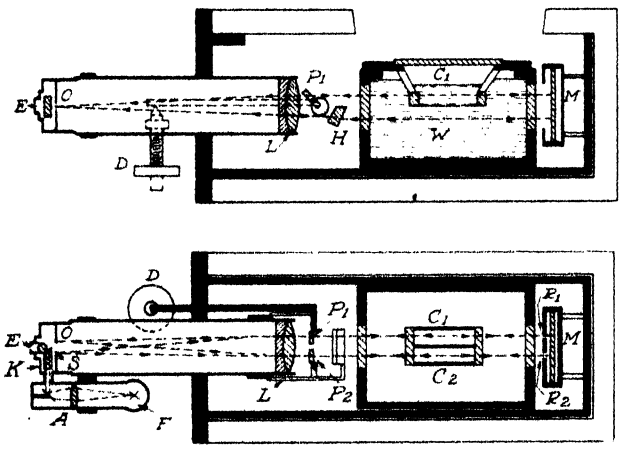


Fig. VIII-9

White light is furnished by the small 4 volt tungsten lamp, F. By means of the lens, A, a mirror and the totally reflecting prism, K, the image of the filament, F, is focused on the narrow slit, S (see Fig. VIII-9, lower half); this slit acts as a (very narrow) secondary source, the light from which is rendered parallel (just as in Fig. VIII-8) by the lens, L. The light then passes through the two compartments, C_1C_2, of the water chamber and the rectangular apertures, R_1R_2, thence to a mirror, M, where the two beams of light are reflected back upon themselves, pass through the water chamber again and finally, by means of the lens, L, are reunited at O, forming a series of interference fringes. These fringes are viewed by the cylindrical ocular, E, which gives a magnification of 50 diameters, but in the horizontal direction only.

Besides the two interfering beams of light already considered, another pair proceed from the slit, S, in a precisely similar way, except that they pass below and not through the chamber, C, likewise forming at 0 a second system of interference fringes. This latter fringe system is (practically) fixed in position; its sole purpose is to furnish a set of fiduciary lines which take the place of the crosshairs ordinarily used as reference marks in optical instruments. Accordingly, if the eye is placed at E, one sees two sets of alternate bright and dark bands, the two sets being separated by a narrow line. In each set of fringes only one of the bright bands is pure white, and the bands adjacent to it are bordered with blue toward the center and with red on the outside; it is this central achromatic band which constitutes the reference point of each system.

One set of bands can be displaced relatively to the other set by tilting the movable inclined plate P_1 (P_2 is fixed); this is effected by turning the micrometer screw with attached drum D, by means of which, therefore, the two achromatic bands can be brought to coincidence, and the corresponding reading on the drum observed.

If water is put in one half of the cell and a dilute solution of salt in the other, the number of scale divisions of displacement will be determined by the difference in refractive indices of the solution and the pure solvent. A calibration curve can be obtained by making up solutions of known concentration and comparing with water. Plotting scale readings against concentration, a line is obtained which is almost straight. The deviation from a straight line is due, not to an inconstant variation of refractive index, but to the fact that a variation of ten scale units at one end of the scale may increase the optical length of the beam more than it would at the other end of the scale. Stated in other words, the thickness of one band varies with the scale division because of properties inherent in the lever arm action. The band thickness may vary as much as 10%. But since this variation is quite regular, a few points will be sufficient for calibration. The range of the 5 mm. chamber is from N_D 1.33320 to 1.34010 for 3000 divisions, using water as the comparison liquid. This corresponds to a range of 15.0 to 33.0 on the immersion refractometer. Assuming that the latter

can be read to 0.05 division, the precision with this particular chamber is about ten times that of the refractometer. With the 40 mm. chamber it would be about 80 times as great, but the range would be one-eighth as great. With this chamber one division corresponds to 1.5 to 3.0 mg. of solute per liter for most aqueous solutions; the greatest differences of concentration which can be directly compared are therefore from 0.45% to 0.90%. The range of the measurement with the interferometer can be increased by comparing the solution against solutions having a known amount of solute present. This does not decrease the precision of the measurement. Thus any concentration of solute can be determined if a series of known solutions has been prepared so that each solution of the series differs by no more than 3000 scale divisions from the preceding one.

There are two procedures which one may follow when using the interferometer for analysis. First, it may be used as a direct reading instrument, as just outlined. A calibration curve is constructed by making up a number of solutions and comparing them with water, preferably the same water as that used in making up the solutions. The readings are plotted against concentration and connected to make a smooth curve. When the unknown is compared with water, its concentration can be read from the curve.

In the other method, the interferometer is used as a zero reading instrument. In this method, no previous calibration is necessary but an approximate knowledge of the concentration of the unknown solution is required. It is then compared with two solutions, one slightly more and one slightly less concentrated. This method is slightly more laborious for a single determination, but one gains in precision what one loses in convenience. This is due to the fact that only a limited portion of the scale is used (the solutions should not differ by more than 200 scale divisions). In addition to not requiring a previous calibration, this method is not subject to the error caused by the apparent shifting of the achromatic band of the interference system. When comparing a solution of a salt with water, it must be remembered that the central band is brought back to its zero position by turning a glass plate. The increase in the refractive index of the liquid is counterbalanced by decreasing the effective thickness of the compensator plate. Since the diffusion power of the solution differs from that of glass, the band system changes its appearance, so that after the concentration of salt has increased sufficiently (usually about 300 scale divisions), there is an apparent shift in the position of the achromatic band which, if not considered, would cause an error of one band width (18 scale divisions). This shows the advantage of working over a very limited portion of the scale.

To secure a precision of $\pm$ 0.000001 with the refractometer, the temperature must be regulated to 0.01°. Since the interferometric method is a differential one, no special regulation of temperature is required in order to determine the difference in N_D of two solutions to 0.0000001. The sensitivity of the instrument, in terms of average parts of solute per million of solvent, in as follows for one scale division:

Refractometer (temperature to 0.01°) . . . . . 200 - 300
Interferometer (simple temperature control). . . 40 mm chamber . . . 1.5 - 3.0

The interferometer is not entirely independent of temperature because there is a slight difference between the temperature coefficients of solution and solvent. Thus, a solution of potassium chloride giving a reading of 200 when compared with water at 25° will give a reading of 202 when both are calculated at 20°. With water solutions a variation of $\pm$0.5° is permissible even in very accurate work. It is absolutely necessary, however, that the two chambers should be at exactly the same temperature. With organic liquids accurate control of temperature is required.

Uses of the Interferometer. The use of the interferometer in analyzing gases has already been mentioned. It has been used to determine the permeability of balloon fabrics to hydrogen and helium. Many applications are possible in the analysis of gases. Using a 1 meter chamber 0.02% of carbon dioxide or methane in air can be determined.

It has been used in the investigation of sea water to chart ocean currents; in the analysis of dilute solutions used for freezing point determinations. It can be used to determine potassium and sodium in a mixture of their sulfates or chlorides with a precision of $\pm$0.1 mg. on a 50 mg. sample. The mixture is dissolved in exactly 200 times its weight of water and compared with a standard solution of pure potassium sulfate dissolved in 200 times its weight of water. The reading will range from 430 to 0 as the composition of the mixture ranges from pure sodium sulfate to pure potassium sulfate and a calibration curve is constructed.

It has been used in water investigations, in

measuring adsorption, in investigating colloidal solutions, sewage, fermented liquids, milk, and in biological problems such as measurement of serums, CO_2 in blood, ethyl alcohol in blood, ferment activity, concentration of heavy water. It has been used in determining the end point in titrations and in following the velocity of reactions. In acidimetric and precipitation reactions it gives as accurate results as good visual methods. It is necessary to plot the straight lines showing the change in reading with solution added; at the end point a sharp angle occurs. The interferometer is particularly valuable in measuring small changes in the composition of mixtures of two organic liquids as a result of preferential adsorption.

LABORATORY DIRECTIONS FOR THE ABBE REFRACTOMETER

1. Be sure that the instrument is clean and in working condition. Make certain that the prisms are clean and dry.
2. Start the temperature controlling device and adjust to $20^{\circ} \pm 1^{\circ}$, or better, if possible.
3. Turn the milled head to separate the prisms. Introduce a drop of distilled water at the funnel-shaped opening between the prisms, or place it on the lower prism and lock the prisms together. Especial care must be taken not to touch or scratch the prism.
4. Set the scale near 1.33. Adjust the light source and mirror or tilt the instrument on its bearing until the illumination is as bright as possible.
5. Adjust the dispersion screw on the telescope so that the dividing line between the light and dark halves of the field is as sharp as possible. If the dividing line is not sharp and the two fields are not readily distinguished from each other, place a sheet of white paper over the mirror. This gives a better source of diffused white light.
6. Move the arm carrying the reading telescope until the dividing line cuts the intersection of the cross hairs. Focus the eyepiece so that the cross hairs are clearly seen.
7. Read the index of refraction on the scale, estimating the fourth place. Focus the reading telescope so that the divisions are clearly discernible. The dispersion may be read on the rotating drum.
8. Turn off the heating element if one is being used and then turn off the water.
9. Open the prisms and clean them with soft tissue moistened with a little alcohol. Do not pour or spill alcohol all over the prisms.
10. Close the prisms and replace the cover on the instrument.
11. Do not change any of the adjustments. The instrument have been adjusted to give correct readings.

BE CAREFUL NOT TO SCRATCH THE PRISMS.

Following the above directions determine the refractive index of a liquid supplied by the instructor. Make five settings and take the average. Suitable liquids are sugar solution, alcohol, or an oil.

LABORATORY WORK WITH THE IMMERSION REFRACTOMETER

This consists in determining the percentage by volume or weight of an unknown ethyl alcohol solution and the grams per 100 ml. of solute in some salt solution. The only data available for a salt at 25° are those shown in Fig. VIII-10, which is a curve constructed

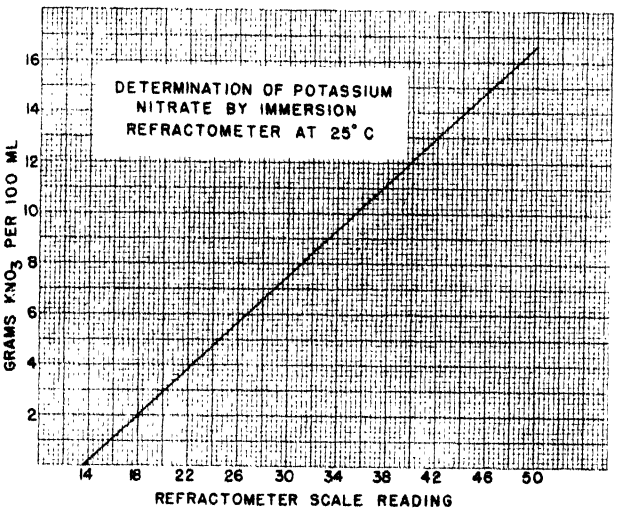


Fig. VIII-10

for potassium nitrate from a large number of student results. For other salts Wagner's data at 17.5°C. must be used.

For volatile liquids the instrument is provided with a metal container constructed with a glass bottom which fits over the prism and locks with a partial turn. It is advisable to use this instead of a beaker when alcohol solutions are used. It is important that the dot on the attachment correspond to the dot above the prism; otherwise the pins will not fit into the slots properly.

The best way to control the temperature in the water bath (see Fig. VIII-5) is to circulate through it, by means of a small centrifugal pump, a stream of water from a large thermostat maintained at the proper temperature. The water bath may be insulated on

the side with sheet asbestos or felt to decrease heat exchange.

1. When a constant temperature has been attained as shown by the protected thermometer in the water bath, place in the holes in the rack provided for this purpose the small beakers of special design containing the solutions to be analyzed, and cover them with crucible covers. Place beside them a beaker of distilled water. The temperature of the latter may be tested with a very small thermometer.
2. When the temperature is constant, place the prism in the beaker of distilled water to attain the proper temperature.
3. Adjust the position of the instrument and of the mirror until the maximum contrast is obtained between the light and dark parts of the field.
4. Adjust the compensator until the dividing line is free from color.
5. Focus by turning the eyepiece until a sharp line is obtained.
6. The reading should be the same as that given in the preceding table (p. *107*). Fractions of a division are obtained by turning the round vernier until the line just coincides with the lower numerical scale division. Make a series of five settings and take the average. If there is a small correction, it is best to note this and apply it in all measurements. If it is considerable, ask the instructor to reset the instrument.
7. It is desirable to keep the prism in distilled water at the proper temperature when not testing a solution, because then it requires less time to reach the temperature of the solution.
8. Remove the prism from the water, wipe it dry with a soft cloth, and place it in the solution to be analyzed. Make a series of readings and take the average.
9. Refer to the proper table to find the concentration corresponding to the reading.
10. Report the concentration and pertinent data to the instructor.
11. Rinse the prism with distilled water of the same temperature and wipe it dry with a soft cloth. Be very careful not to scratch the prism.

Notes: If a wavy border line is obtained, the temperature of the prism is not uniform.

It is well to take the temperature in the beaker before and after the readings in a given solution. It is recommended to use the volatile liquid container instead of an open beaker for alcohol solutions.

Use either artificial light or daylight, whichever is more convenient.

A change in reading shows that the temperature is changing.

Do not remove the prism.

This is an expensive instrument. Be careful with it.

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CHAPTER IX

THERMAL CONDUCTIVITY AND OTHER METHODS FOR THE ANALYSIS OF GASES

Four methods for the analysis of gases - thermal conductivity, gas density, heat of combustion, and velocity of sound in a gas - are grouped in this chapter. These four methods are only a selection of the possibilities. Many of the methods discussed elsewhere can also be used for the determination of certain gaseous constituents. Among these are the interferometer, infrared spectrophotometers, visual or ultraviolet spectrophotometers, and the mass spectrometer.

Thermal Conductivity.

The thermal conductivity of a gas is defined as the quantity of heat transferred in unit time between two unit surfaces in a gas when they are unit distance apart and the temperature difference between the surfaces is 1^{o}. In the metric system the units will be calories, square centimeters, centimeters, and degrees centigrade. At atmospheric pressure, the thermal conductivity of a gas is quite insensitive to changes in pressure and is a function of the composition. At pressures in the range of 10^{-2} to 10^{-5} mm. of Hg, the thermal conductivity is very sensitive to pressure changes and forms the basis of the Pirani gauge method for determining such pressures.

Absolute values of the thermal conductivity are seldom needed for analytical purposes. The thermal conductivity of the gas mixture to be analyzed is usually compared with that of some reference gas, such as hydrogen, nitrogen, or wet or dry air. The calibration of the equipment is empirical.

The apparatus required is simple. A fine wire, usually platinum or some other metal or alloy with a high temperature coefficient of resistance, is stretched along the axis of a metal or glass cylinder. Either two similar cylinders and two resistances or four similar cylinders are used to form the arms of a Wheatstone bridge circuit. When a current is passed through the bridge the wires become heated. The final equilibrium temperature of the wire depends upon the thermal conductivity of the gas surrounding it; the higher the conductivity the lower the temperature. If the gases in the cells are the same, the wires will reach the same temperature and, therefore, will have the same resistance; thus the bridge is balanced. If, on the other hand, the gases are different, the final temperatures and resistances of the wires will be different and the bridge will be unbalanced. The extent of unbalance of the bridge may be measured by a galvanometer or a potentiometer and can be calibrated in terms of composition of the gas. The bridge could also be balanced by varying one of the resistances if only two cells were used. A typical circuit employing four thermal conductivity cells and a potentiometer or galvanometer to indicate the unbalance condition of the bridge is shown in Fig. IX-1. A photograph of a typical thermal conductivity unit containing four cells mounted in a housing is shown in Fig. IX-2.

A well-matched unit will not show perceptible change in the balance condition if the cells are filled with the same gas and the operating current is varied by ± 10 milliamperes from the normal. Also, a variation of as much as 50^{o}C. in the temperature of the block should not affect

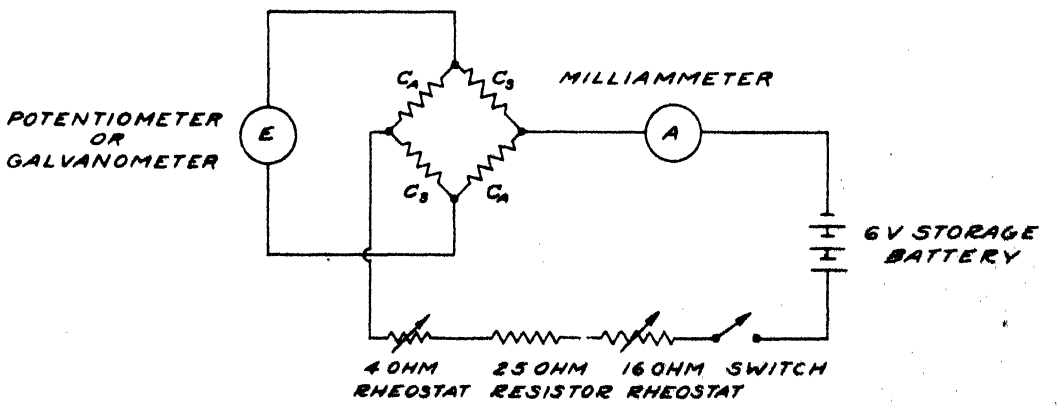


Fig. IX-1. Wiring diagram for Thermal conductivity unit. C_A, analysis cells. C_S, standard cells

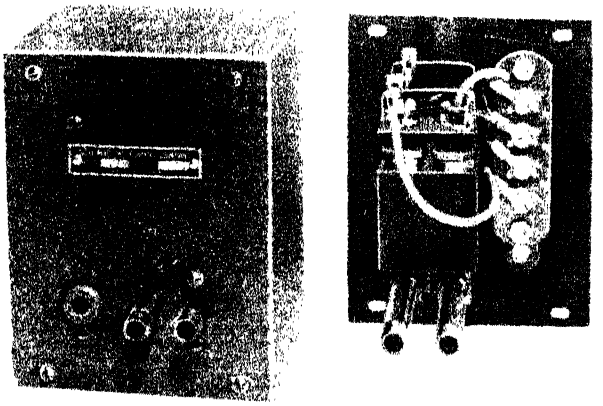


Fig. IX-2. Gow-Mac Thermal Conductivity Unit (Courtesy of Gow-Mac Instrument Co.)

the balance condition. Glass cells must be used when corrosive gases are to be measured.

Since the off-balance condition can be measured by a recording potentiometer, it is possible to make the thermal conductivity method either continuously recording, or controlling, or both. Either a constant current can be furnished to the bridge circuit or a constant potential can be applied to the input terminals of the bridge. The latter is usually more convenient when a recording potentiometer is used to indicate the off-balance condition or when the gas composition changes rapidly. Daynes[1] discusses the various circuits and also the theory of the method in his excellent monograph.

The thermal conductivity method is easily applied to the determination of the composition of a binary mixture provided that the two gases have different thermal conductances. The greater the difference between the two gases, the greater the sensitivity of the method. A multicomponent mixture can be treated as a binary mixture if all components but one remain constant or if all of the gases except one have nearly the same thermal conductance. There are a few binary mixtures, however, that exhibit maxima in the conductance-composition relationship. Such mixtures - for example, air-water, air-ammonia, air-butane - can be determined only if one knows on which side of the maximum the composition lies.

Multicomponent mixtures can frequently be determined using a differential method. In this procedure a thermal conductivity unit is necessary for each component. The gas is passed through one half of one unit, through a chemical reagent to remove one constituent, and then through the second half of the first unit. Thus the gas is compared with itself after removal of one constituent and the difference in thermal conductivity will be due to the constituent removed. The procedure can be continued until all of the components are determined.

The thermal conductivity method has been applied to the determination of carbon dioxide in air, sulfur dioxide in air, acetone vapor in air, air in helium or hydrogen of balloons, internal combustion exhausts, flue gas, the gases resulting from the Fischer-Tropsch synthesis, etc.

1. Daynes, H. A., "Gas Analysis by Measurement of Thermal Conductance," Cambridge University Press, London, 1933.

Gas Density

The measurement of the density of a gaseous mixture is useful in determining the composition of binary mixtures. Multicomponent mixtures can be partially analyzed provided that all components but one remain constant or have nearly the same density. As would be expected, the measurements are more precise when the densities of the two gases are quite different. The density of an ideal gas is directly proportional to the molecular weight and the possibility of precise determinations can be predicted for the molecular weights of the constituent gases.

Many types of instruments have been devised for the measurement of the density of gases. The Edwards gas density balance shown in Fig. IX-3 depends on the measurement of the pressure required to bring a float to an equilibrium position at a constant temperature. The rate of effusion of a gas through a small orifice is a measure of the density since, at constant temperature:

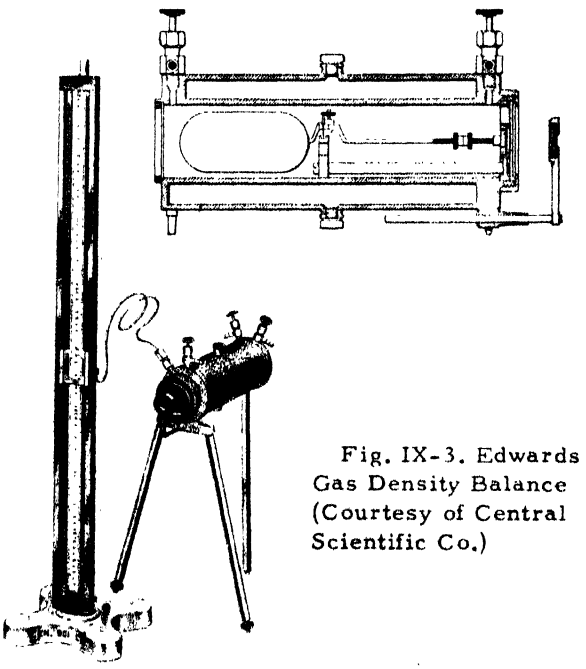


Fig. IX-3. Edwards Gas Density Balance (Courtesy of Central Scientific Co.)

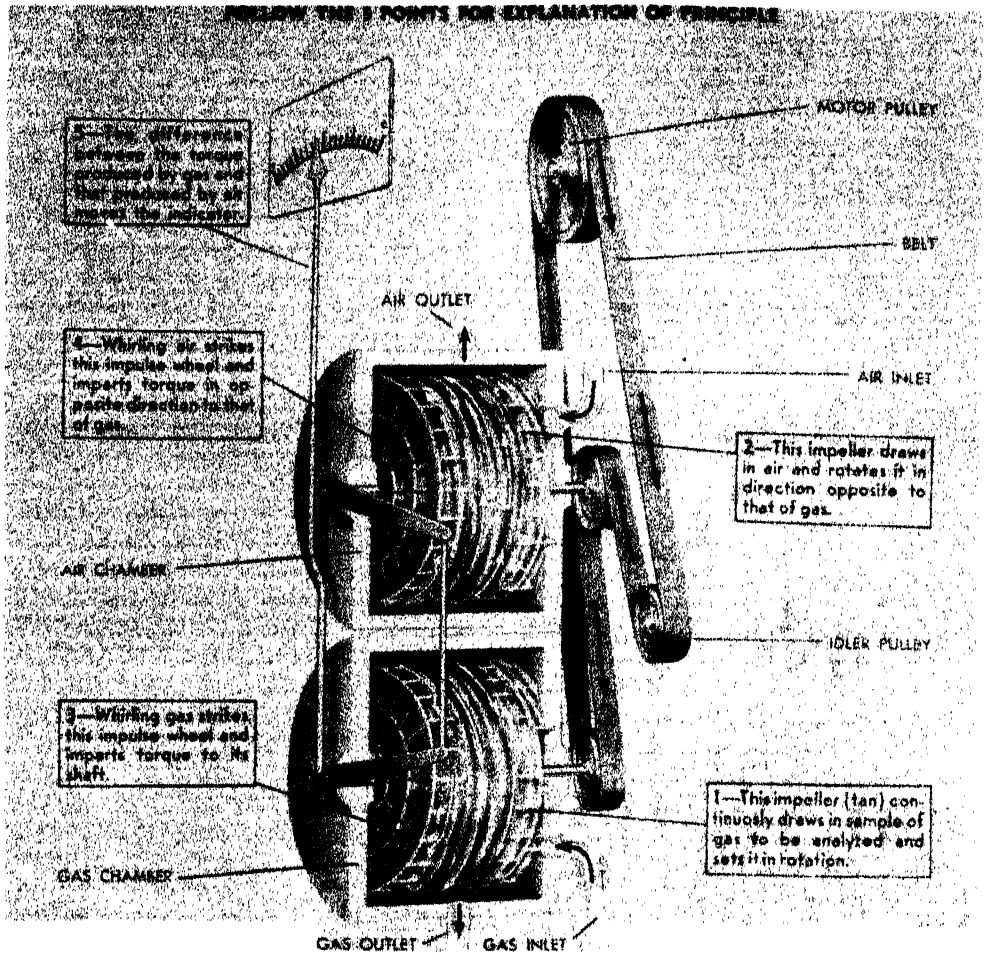


Fig. IX-4. Principle of the Ranarex Specific Gravity Indicator (Courtesy of the Permutit Co.)

$$1/2\ nmv^2 = RT = K \qquad (1)$$

where n = number of molecules;
m = mass of gas molecules;
v = velocity of molecules;
R = gas constant;
T = absolute temperature;
K = constant;
ρ = density;

and $$\rho \propto m \qquad (2)$$

therefore $$v \propto \sqrt{\frac{1}{\rho}} \qquad (3)$$

The Ranarex specific gravity indicator operates on an interesting principle. The gas is given a rotating motion by means of an impeller fan. This fan drives the gas against the blades of an impulse wheel producing a torque. The greater the density of the gas the greater the coupling between the two wheels and the greater the torque produced on the second wheel. In order to eliminate changes in fan speed, temperature, humidity, and atmospheric pressure, a comparing set of wheels is used with air as the reference gas. The two fan wheels are run by the same motor but in opposite directions. The two torque wheels are mechanically coupled to each other and the difference in torque is registered on a dial. The dials may be calibrated directly in percentage of constituent sought or in specific gravity units. Automatic recording and control can be provided for, if desired. The principle and design of this device are further illustrated in Figs. IX-4 and IX-5.

Heat of Combustion

The heat of reaction evolved by a gas when it burns at a filament or in the presence of a catalyst can be used to determine combustible gases in a mixture. One device used for the detection of explosive gas mixtures is quite similar in

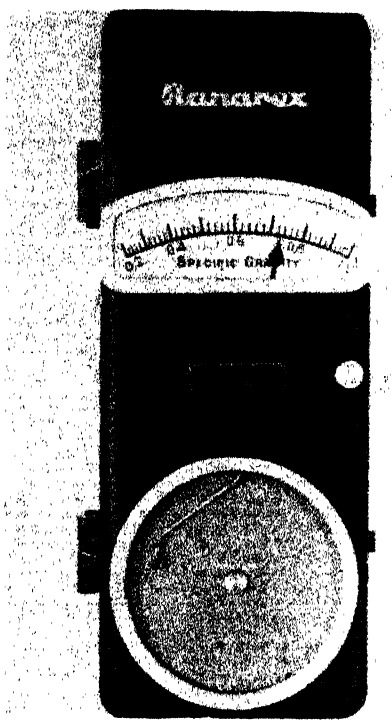


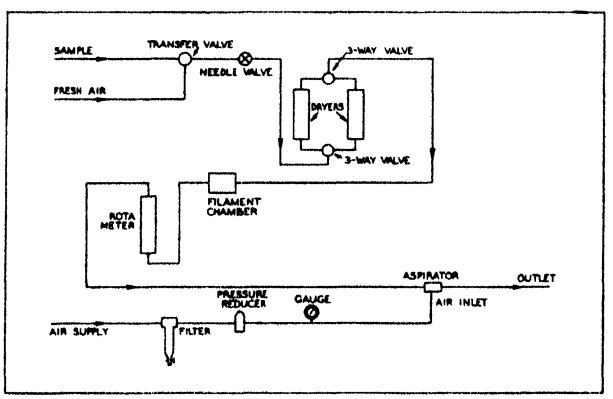
Fig. IX-5. Ranarex Specific Gravity Indicator and Recorder (Courtesy of the Permutit Co.)

age of alcohol, ether, methane, carbon monoxide, or other combustible gas. One commercial example of such a device is illustrated in Figs. IX-6 and IX-7.

Another type of instrument measures the increase in temperature as the combustible gas is burned in contact with a catalyst. An instrument for determining the concentration of carbon monoxide in air is illustrated in Fig. IX-8. The gas is drawn in by a motor through a flowmeter to insure a constant rate of flow. The sample passes through a dehydrating agent to remove water vapor and finally through a bed of "Hopcalite" catalyst[2] which promotes the oxidation of the carbon monoxide to carbon dioxide. The heat liberated by this oxidation is proportional to the concentration of carbon monoxide. Two thermocouples are employed - one in the incoming gas stream and one imbedded in the catalyst - to measure the heat evolved. Such instruments are very sensitive. The range of the instrument shown in Fig. IX-8 is from 0 to 0.15%. The scale is calibrated to 0.005% and can be estimated to 0.001%.

Velocity of Sound in Gases

The velocity of sound in a gas is given by the following equation:



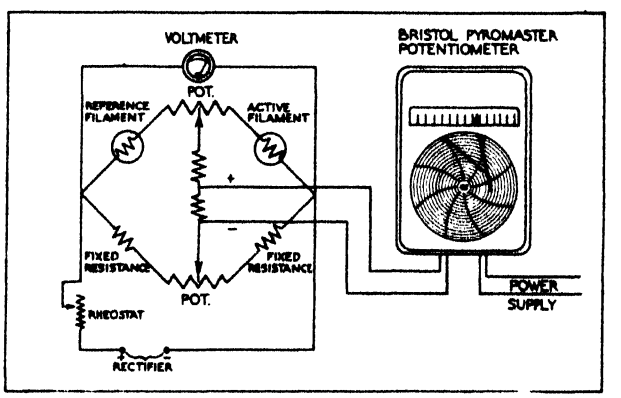


Fig. IX-6. Principle of operation of the Bristol Combustible Gas Recorder (Courtesy of the Bristol Company)

construction to the thermal conductivity apparatus. The gas is passed through a cell containing a heated filament. The combustion of the gas raises the temperature and the resistance of the filament as compared to that of a reference filament. The reference and active filaments form two arms of a Wheatstone bridge circuit. The degree of unbalance of the bridge furnishes a measure of the concentration of combustible gas. The scales can be calibrated directly in percent-

$$v = \sqrt{\frac{\gamma P}{\rho}} \qquad (4)$$

where v = velocity;
P = pressure;
ρ = density;
$\gamma = \frac{Cp}{Cv}$, the ratio of the specific heats at constant pressure and constant volume.

2. A mixture of Ag_2O, Co_3O_4, and MnO_2.

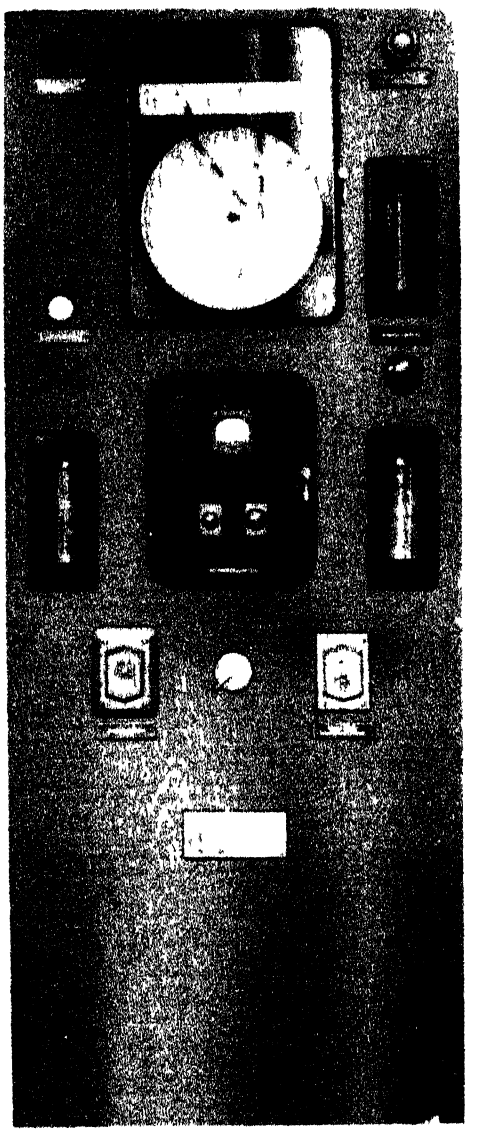


Fig. IX-7. Bristol Combustible Gas Recorder (Courtesy of the Bristol Company)

The ratio of the specific heats, γ, depends somewhat on the nature of the gas, being 1.67 for a monatomic gas and somewhat lower, averaging around 1.3 for polyatomic gases. This is not a great variation and, for most gases or gas mixtures, can be assumed to be essentially a constant. If we substitute in equation (4)

$$\frac{nM}{V} = \rho \qquad (5)$$

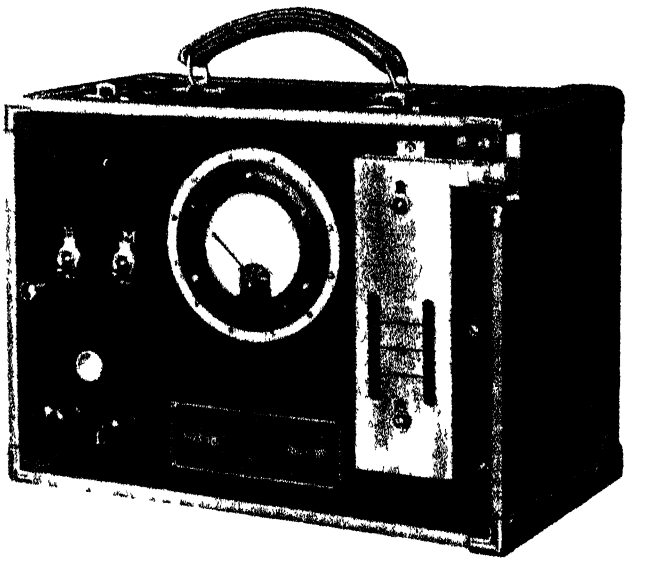


Fig. IX-8. Mine Safety Appliances Carbon Monoxide Indicator (Courtesy of Mine Safety Appliances Co.)

where n = number of moles;
M = molecular weight;

we obtain the following relationships:

$$v = \sqrt{\frac{\gamma PV}{nM}} \qquad (6)$$

or since

$$PV = nRT = nK$$

where K = a constant, if T remains constant,

$$v = \sqrt{\frac{\gamma K}{M}} \qquad (7)$$

$$v \propto \sqrt{\frac{1}{M}} \qquad (8)$$

Thus, the velocity of sound in a gas is practically proportional, at constant temperature, to the reciprocal of the square root of the molecular weight. The molecular weight must be interpreted as the average molecular weight for a

gaseous mixture.

Diehl and Crouthamel[3] have devised an apparatus which can be used for the rapid analysis of gases by the above principles. Their apparatus consists of a long tube in one end of which is affixed a small microphone connected to an amplifier and a signal strength measuring meter. In the other end of the tube is placed a small speaker connected to a signal generator whose frequency can be varied continuously by a calibrated condenser.

Whenever the frequency is such that a standing wave is set up in the tube with the microphone pickup at an antinode, the signal received will be at a maximum. The signal is a minimum when the frequency is such that the pickup unit is at a node.

When the wavelength, λ, is a constant, as it is in the device where the tube length is fixed, the wavelength is adjusted until both microphone and hummer are at antinodes. Under this condition the frequency, ν, is proportional to the velocity. This follows from the relationship:

$$\nu\lambda = v \qquad (9)$$

The tube is filled with the gas sample and the frequency adjusted until the indicating meter shows a maximum signal. The position of the condenser is then read and plotted against concentration. After calibration with known samples in the usual manner, the instrument can be used to determine unknowns.

LABORATORY WORK WITH THE THERMAL CONDUCTIVITY METHOD

A determination of the percent of carbon dioxide in air will be used as an example of the thermal conductivity method. Dry air is used as the reference standard although wet air could be used equally well. Carbon dioxide has a lower thermal conductivity than air. Since the composition of the air remains constant, the carbon dioxide-air mixture will be treated as a binary mixture.

Apparatus Required

Gow-Mac Ever-Tite Thermal Conductivity Unit, preferably Model B/T.

6 volt storage battery.

0-250; 0-500 or 0-1000 D.C. milliammeter.

Potentiometer.

1 low resistance (about 6 ohm) potentiometer-type variable resistor.

1 variable resistance (about 20 ohm).

1 variable resistance, about 4-10 ohms.

1 fixed resistor, about 20-30 ohms.

(The above resistors must be capable of carrying a current between 250 to 500 milliamperes.)

Gas handling system.

Procedure.

1. Connect the parts as indicated in Fig. IX-1.
2. Fill the capped tube for the reference cells with a drying agent, such as magnesium perchlorate, silica gel, or drierite (do not use calcium chloride); insert a small plug of glass wool and screw the free end into the reference cell outlet. Close the other end of the reference cell outlet with the plug provided with the unit.
3. Adjust the current through the circuit to 138 milliamperes for the B/T unit, or to the recommended value for the unit employed, by adjusting the variable resistances. Maintain this current throughout the experiment.
4. A drying tube containing the same desiccant as was sealed into the reference cells should be placed before the analysis cells.
5. Pass dry air slowly through the analysis cells and adjust the resistor at the end of the Wheatstone bridge (the 6 ohm resistor) until a balance is obtained. Balance is indicated by a zero potential reading on the potentiometer.
6. Synthesize a sample containing about 1% carbon dioxide by volume and pass it slowly through the analysis cells. If only a small sample is available, the sample may be trapped in a balloon or in a gas absorption pipet and returned through the cells. Measure the off-balance potential on the potentiometer when equilibrium is reached.
7. Synthesize several other carbon dioxide-air mixtures containing up to about 10% of carbon dioxide and measure the corresponding potentials on the potentiometer.
8. Plot potential against concentration of carbon dioxide.
9. Obtain an unknown sample and measure the potential of the bridge when the unknown is passed through the analysis cells. Determine the percentage of carbon dioxide from the calibration curve for the instrument.

Note: A convenient and simple gas handling system can be constructed from a gas buret and a large, round-bottomed flask (for example, 1 liter capacity). Place a two-hole stopper in the

3. Diehl, H. and Crouthamel, Private Communications.

flask and fit one hole with a capillary stopcock reaching to the bottom of the flask. Fit the second hole with a capillary stopcock reaching just below the stopper. Measure the volume of the flask up to the stopper by filling with water and pouring into a graduated cylinder.

A gas sample is prepared by first flushing the flask with carbon dioxide-free air, evacuating the flask slightly with a water pump and admitting from the gas buret a measured volume of carbon dioxide through the short stopcock. The stopcock is opened momentarily to the air through a soda-lime tube to equalize the pressure. The gas sample is forced through the analysis cells by admitting through the long stopcock a retaining liquid such as mercury or a saturated salt solution containing a few drops of hydrochloric acid per liter.

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CHAPTER X

MASS SPECTROMETRY

The mass spectrometer, although known for some time, has only recently been widely used as a routine analytical tool. As the name indicates, the instrument sorts out ions according to their masses, or, more strictly speaking, according to the ratio of charge to mass, e/m. In a mass spectrograph the ions are brought to focus on a photographic plate and in the modern mass spectrometer the ionic species are brought successively to focus on a fine exit slit and collected in a device which can measure the intensity.

Assortment of ions according to their ratios of e/m is accomplished by combination of electrical and magnetic fields. In Fig. X-1 is illustrated the relationship of the fields in a mass spectrometer of the 180 degree or Dempster[1] type. Between A and B there is an electrical field only, so that the ions move in straight lines and those passing through the slit would have the kinetic energy as given by the equation:

$$1/2\ mv^2 = eV \qquad (1)$$

where m = mass of the ion;
v = velocity;
e = charge of the ion;
V = accelerating voltage.

When the ions leave the electrical field they pass into a magnetic field. Since charged particles moving in a magnetic field experience a force at right angles to the direction of the field and the direction of motion, they move in circles. Equating the centripetal and centrifugal forces on such an ion, one obtains the relationship:

$$\frac{mv^2}{r} = Hev \qquad (2)$$

where H = strength of magnetic field;
r = radius of curvature of path of the ion.

Solving both equations (1) and (2) for v and combining the two, one obtains equations (3) and (4).

$$\frac{e}{m} = \frac{2V}{H^2r^2} \qquad (3)$$

$$r = \sqrt{\frac{2V}{H^2} \cdot \frac{m}{e}} \qquad (4)$$

Thus the radius of curvature of the particle in the magnetic field depends on V, H, and the ratio of $\frac{m}{e}$. In the 180 degree mass spectrometer, r is fixed, so for any given values of V and H, only particles with a certain ratio of $\frac{m}{e}$ would impinge on the collector. Either the voltage, V, or the strength of the magnetic field, H, could be varied in order to cause particles with other ratios of $\frac{m}{e}$ to fall on the collector.

Before neutral atoms or molecules can be sorted on a mass spectrometer, they must be ionized. In the spectrometers designed for the analysis of hydrocarbons and similar substances, ionization is accomplished by bombarding the molecules in the gas phase with a stream of electrons emitted from a hot, oxide-coated filament. These electrons may knock other electrons out of the molecule, leaving positively charged ions; or they may decompose the molecule into charged fragments. Determination of the kinds of molecules present depends on the fact that each kind of molecule decomposes in a definite manner, always giving, on the average, a definite distribution of decomposition products.

Instruments. Fig. X-2 shows a diagrammatical sketch of a commercial mass spectrometer manufactured by the Consolidated Engineering Corporation. Molecules in the vapor phase under a pressure of about 40 μ, either from a gaseous sample or from a sample with an appreciable vapor pressure, pass through the precision restriction, R, into the ionization chamber

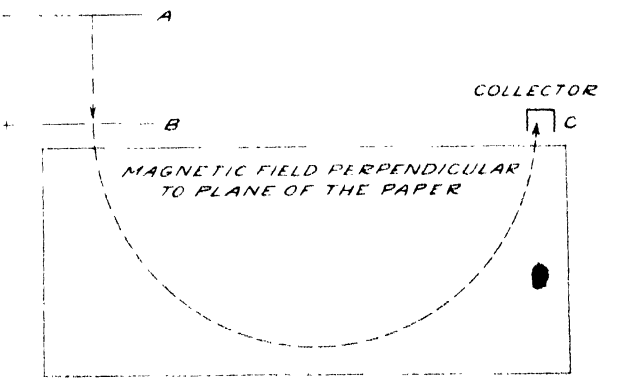


Fig. X-1. Relationship of electrical and magnetic fields in a mass spectrometer of the Dempster type

1. Dempster, A. J., Phys. Rev., 11, 316 (1918).

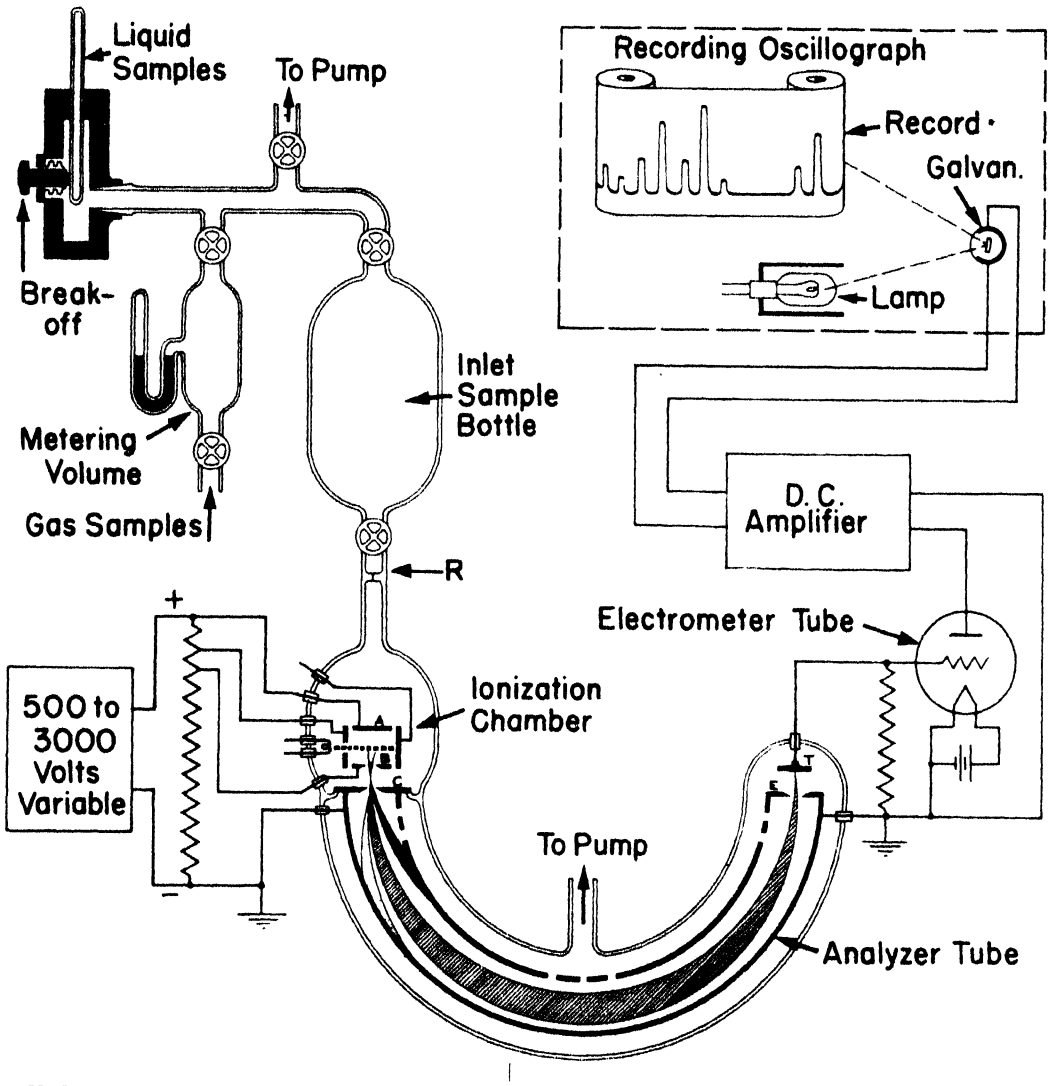


Fig. X-2. Diagrammatical sketch of a mass spectrometer and associated apparatus

where a much higher vacuum (10^{-6} mm.) is maintained to prevent intermolecular collisions. In the ionization chamber the gas molecules are bombarded by a stream of electrons (dotted line).

The ions formed by the electron bombardment leave the ionization chamber through a narrow vertical slit, B, and are accelerated to a high velocity by a strong electrostatic field of 500 to 3000 volts between slits B and C. A strong, constant magnetic field of about 3500 gauss diverts the fast moving ions into circular paths. Only those ions with the correct radius will strike the collector plate, or Faraday cage, T. The other ions will hit the analyzer tube at some point, be neutralized, and be pumped away. By varying the accelerating voltage between the slits B and C, ions of each specific mass, $\frac{m}{e}$, can be made to strike the plate. This variation can be controlled manually or automatically at a regulated rate. The current due to the charges given up to the collector plate by the ions is amplified by a direct-current feed-back amplifier, and the output is fed through four galvanometers with different sensitivities connected in series. The positions of the galvanometer mirrors are photographically recorded on a sensitive paper on a revolving drum. A sort of "spectrum" showing the relative abundance of the various ionic species is obtained.

By the use of four separate galvanometers with relative sensitivities of 1, 3, 10, and 30, spectrum peaks varying in height from 0.2 to 3000 arbitrary divisions may be significantly read on the 8-inch photographic record paper. This enables the height of any peak to be

recorded within better than 1% accuracy over a range of magnitude of 1 to 250. Accurate zero adjustments of the recording galvanometers is not required, as peak heights are determined by the difference between the normal trace and the top of the peak.

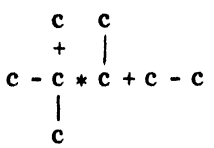
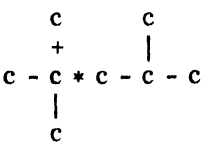
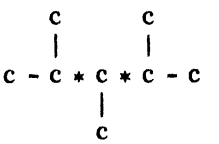
The change in the accelerating voltage is accomplished by decreasing the charge placed between slits B and C. As the potential decreases a progression of masses from light to heavy is brought to focus. The peaks representing the individual mass units in a spectrum are identified on the record by marks produced by a light, which is flashed at predetermined levels of accelerating voltages.

For masses up to 100, good resolution is obtained from low accelerating voltages and weak magnetic fields, and since broad collimating slits may be used, strong ion beams results. Heavy ions require narrow slits resulting in smaller ion beams and necessitating stricter alignment. However, the analysis of heavy ions is more often limited by low vapor pressure.

The difficulty of producing a strong, uniform, and unvarying magnetic field over a large area makes the magnet the most important component of a mass spectrometer. Large magnets are expensive to construct and usually require several kilowatts of power. Thus large power supplies, generally motor generators with sensitive electronic regulators, are required.

The electron beam from the hot filament is accelerated through a potential of 50 volts. The ionization potentials of most hydrocarbons are around 9 to 14 volts, so that both ionization and dissociation occur. As sufficient molecules are present and dissociated for the probability law to hold, the dissociation fragments will always occur in the same relative abundance for any given compound. The relative abundance of the various masses resulting from this dissociation becomes a sort of "fingerprint" for each compound. For example, consider three paraffins of similar structure: namely, 2,2,3-trimethylpentane, 2,2,4-trimethylpentane, and 2,3,4-trimethylpentane. Table 1 indicates the relative abundances of the fragments produced by bombardment of three trimethylpentanes. In the structural formulas the asterisk indicates the bond which is broken in the most probable process of ionization, and the plus sign indicates the next most probable process. The mass numbers for which ion abundances are shown are 114, which corresponds to the positive ions formed by the loss of an electron only; mass 99, corresponding to the loss of a methyl group plus an electron; mass 71, corresponding to the loss of a propyl group plus an electron; mass 57, corresponding to the loss of a butyl group plus an electron; and mass 43, corresponding to the loss of an amyl group plus an electron. The conditions of bombardment must be carefully controlled; therefore all critical currents and voltages are electronically monitored.

TABLE 1. PRODUCTS OF IONIZATION OF TRIMETHYLPENTANES[2]

	Relative Abundances of Mass Spectra		
	2,2,3-Trimethylpentane	2,2,4-Trimethylpentane	2,3,4-Trimethylpentane
			
Mass Number			
114	0.1	0.02	0.3
99	3	5	0.1
71	1	1	40
57	70	80	9
43	15	20	50

2. Washburn, H. W., Wiley, H. F., Rock, S. M., and Berry, C. E., Ind. Eng. Chem., Anal. Ed., 17 75 (1945).

The complete unit of the Consolidated Engineering Corporation is shown in Fig. X-3. Another commercially available instrument of the

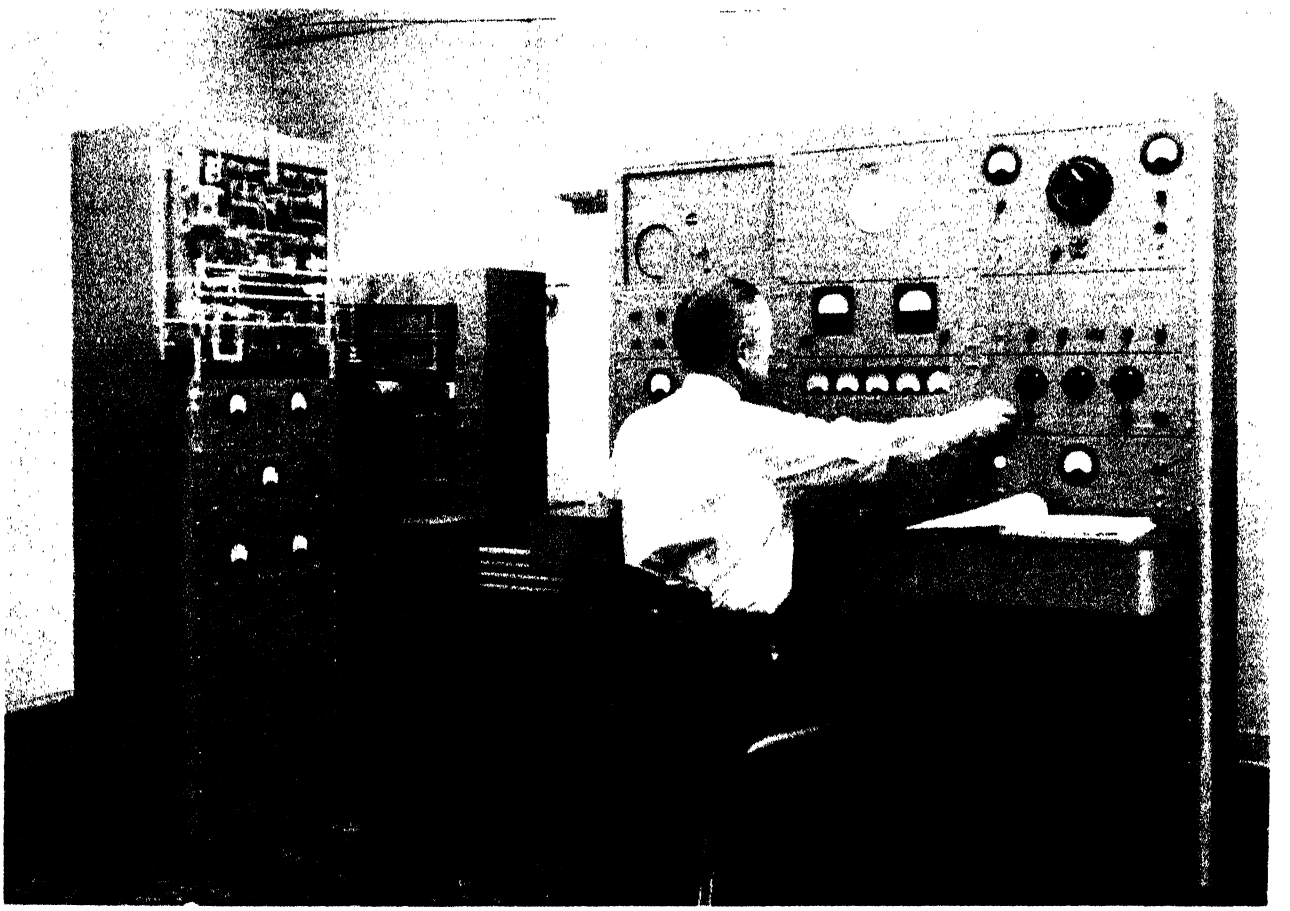


Fig. X-3. Consolidated Mass Spectrometer (Courtesy of Consolidated Engineering Corporation)

same general features and built by the Process and Instruments Company is shown in Fig. X-4. This latter instrument is a 60 degree type with optimum resolution in the biochemically important range up to mass 100. Scanning is manually controlled.

The instrument manufactured by the General Electric Company, and shown in Fig. X-5, operates on a different principle. Instead of maintaining a constant magnetic field, as is done in the two former instruments, the magnetic field is varied to sweep over a mass range of 1 to 300 in a single setting of accelerating voltage. By this method it is claimed that a wider mass range with a more constant sensitivity can be scanned.

Analysis of Mixtures. In order to compute the analysis of a mixture from its composite spectrum, it is necessary to know the individual mass spectra of all the components. These spectra are obtained by running samples of the pure gases through the instrument and, from the individual spectra found, one calculates "the per cent of the compound per division of height of ion current." The method of computation and how the unused peaks may be used to check the accuracy of an analysis are best shown in Table 2, which gives the data and analysis of a depropanizer overhead gas. This table is shown on the following page.

In the first column are listed the masses at which peaks occur on the mass spectrum of the unknown mixture. In the second column are recorded the peak heights read from the automatic record of the mixture. All spectra must first be normalized mathematically to a standard sample pressure before proceeding with the computations. The only components contributing to peaks at mass 57 and 58 are n- and iso-butane, the percentages of which are computed from simultaneous equations shown at the bottom of the table. In these equations the underlined numbers are taken from calibration records obtained by running pure n- and iso-butane individually. From the percentages of the two butanes and from their

TABLE 2. ANALYSIS OF DEPROPANIZER OVERHEAD BY THE MASS SPECTROMETER[3]

m/e	Mixture Peaks	n-Butane	iso-Butane	Propane	Ethane	Methane	Sum of Component Spectra	Residuals
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
15	167.3	1.0	1.6	30.4	23.0	110.3	166.3	+ 1.0
16	134.4	0.0	0.0	0.9	0.8	132.7	134.4	0
26	146.1	1.6	0.9	37.6	106.4	.....	146.5	- 0.4
27	361.6	10.8	12.1	183.0	158.0	.....	363.9	- 2.3
28	777.8	9.3	1.2	275.3	494.4	.....	780.2	- 2.4
29	593.1	12.5	2.6	467.8	105.6	.....	588.5	+ 4.6
30	130.0	0.3	0.0	10.0	119.7	.....	130.0	0
31	2.4	.....	.....	.....	2.5	.....	2.5	- 0.1
38	24.0	0.5	1.2	21.9	.....	.....	23.6	+ 0.4
39	98.0	4.3	8.7	84.6	.....	.....	97.6	+ 0.4
40	14.7	0.6	1.3	13.0	.....	.....	14.9	- 0.2
41	94.1	9.0	18.9	65.8	.....	.....	93.7	+ 0.4
42	49.9	3.9	15.6	30.2	.....	.....	49.7	+ 0.2
43	207.4	32.2	49.8	124.5	.....	.....	206.5	+ 0.9
44	145.3	1.0	1.6	142.7	.....	.....	145.3	0
45	4.6	0.0	.....	4.6	.....	.....	4.6	0
50	0.6	0.3	0.3	.....	.....	.....	0.6	0
51	0.5	0.3	0.3	.....	.....	.....	0.6	- 0.1
52	0.1	0.1	0.1	.....	.....	.....	0.2	- 0.1
53	0.6	0.3	0.3	.....	.....	.....	0.6	0
54	0.1	0.1	0.0	.....	.....	.....	0.1	0
55	0.7	0.3	0.2	.....	.....	.....	0.5	+ 0.2
56	0.5	0.3	0.2	.....	.....	.....	0.5	0
57	2.5	0.9	1.6	.....	.....	.....	2.5	0
58	5.0	3.8	1.2	.....	.....	.....	5.0	0
59	0.2	0.2	0.0	.....	.....	.....	0.2	0

In the calculations below, the underlined figures in the table are used. The underlined coefficients are obtained from previous calibrations.

Computation of mole percentage of n-butane and isobutane

from peak 57: $\underline{0.503}\ p_n + \underline{0.654}\ p_i = 2.5$ (5)

from peak 58: $\underline{2.10}\ p_n + \underline{0.498}\ p_i = 5.0$ (6)

(where p_n = per cent n-butane and p_i = per cent isobutane) n-butane = 1.8 mole per cent and isobutane = 2.4 mole per cent.

Propane (145.3-1.0-1.6)$\underline{0.269}$ = 38.4 mole per cent (7)

Ethane (130.0-0.3-0-10.0)$\underline{0.3175}$ = 38.0 mole per cent (8)

Methane (134.4-0-0-0.9-0.8)$\underline{0.146}$ = 19.4 mole per cent (9)

calibration spectra, their contributions to each of the other masses listed can be readily computed. These values are shown in the third and fourth columns. The small peak at mass 59 is due to the natural presence of butane containing C^{13}.

[3]3. Washburn, H. W., Wiley, H. F. and Rock, S. M., Ind. Eng. Chem., Anal. Ed. 15, 541 (1943).

If now the mass 44 contributions of the two butanes are subtracted from the mixture 44 peak, the remaining amount is due entirely to propane. The percentage of propane in the mixture is computed from this remainder peak and from the sensitivity of the 44 peak to propane. This simple calculation is shown in equation (7) from Table 2, where the underlined value, 0.269, is the sensitivity in per cent per division obtained from the propane calibration. Similar steps are

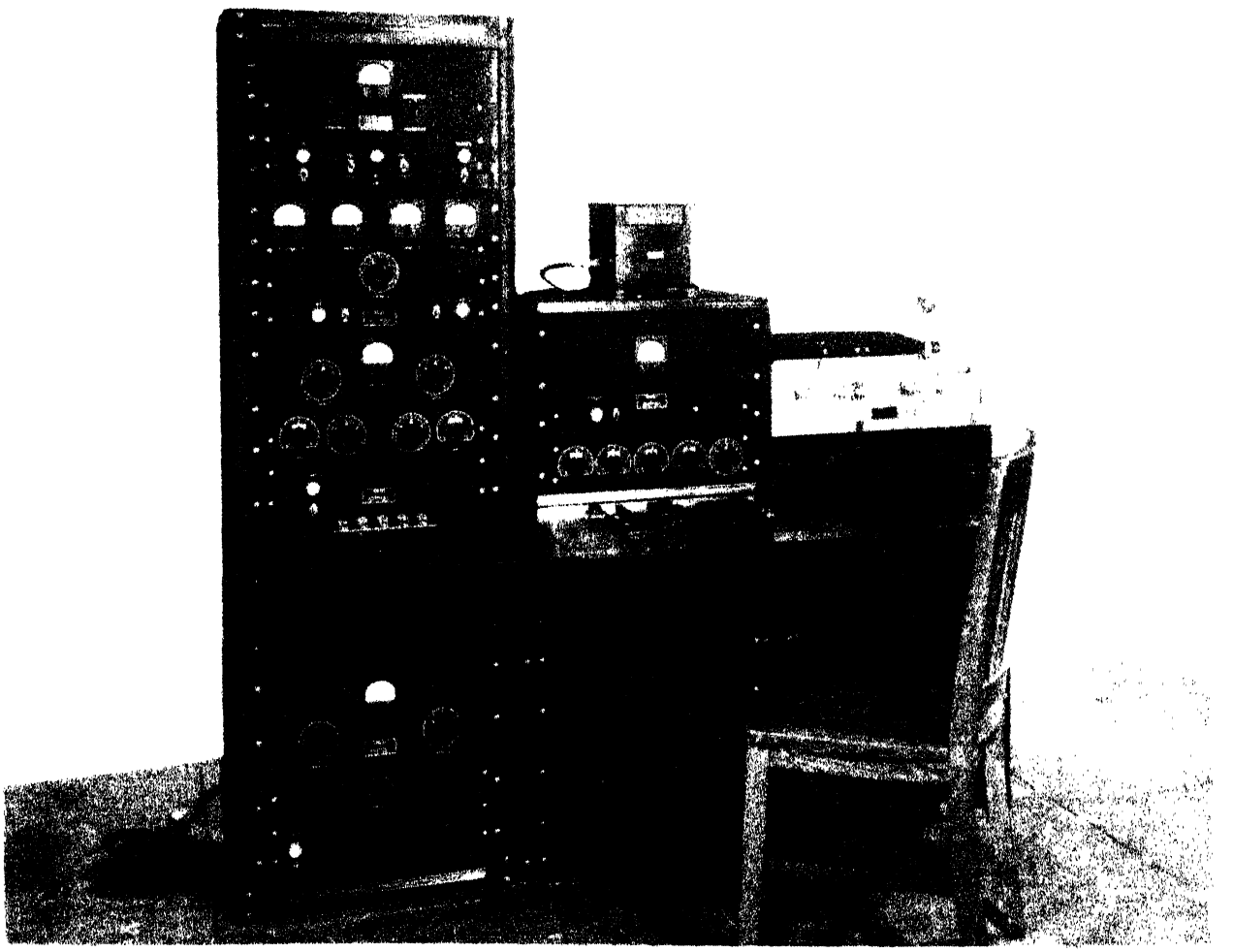


Fig. X-4. Process and Instruments' Mass Spectrometer Model M60
(Courtesy Process and Instruments Company)

used in calculating the remainder of the materials present.

If the apparatus were perfect, if there were no errors in the computations, and if all constituents in the mixture were taken into account, the sum of these component spectra (column 7) would be equal to the mixture peak. The comparison of the sums of the component spectra for each mass with the mixture peak of the corresponding mass therefore offers an excellent check on the reliability of analysis (column 8). One advantage of this method is its ability to detect unexpected components by the relatively large residuals which would be obtained assuming that these constituents had not been in the mixture.

The relative quantity of any particular ionized fragment resulting from the bombardment of a group of identical molecules is a function of the ease with which such a fragment may become separated from the molecule. This in turn is largely dependent upon the atomic architecture of the molecule, a fact which makes possible the separation of isomers - molecules identical in mass, but not in structure.

Electron bombardment of a mixture of gases frequently results in the creation of ionized fragments of identical masses although produced from different species of molecules. However, under the proper conditions each type of molecule produces its own characteristic spectrum of ionized fragments completely independent of all other substances present, and to an extent proportional to the partial pressure exerted by that type of molecule. Thus, the mass spectrum of a mixture of gases is a linear superposition of the spectra of all the components present, and is so treated in the analytical computations.

When two or more substances in a mixture,

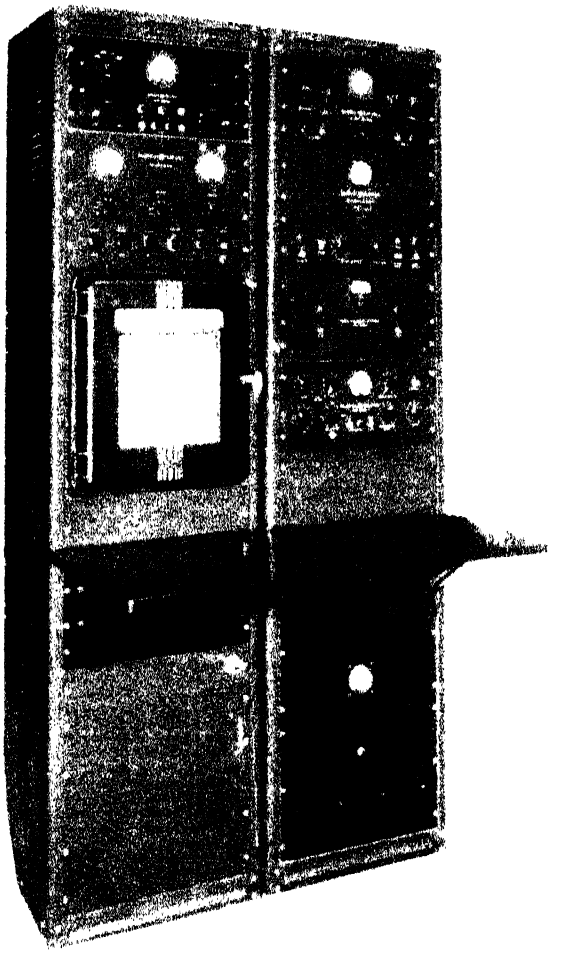


Fig. X-5. G-E Analytical Mass Spectrometer (Courtesy of General Electric Company)

generally two isomers, give the same mass peaks in their spectra, it is necessary to resort to simultaneous equations to determine each component. It is possible to determine each isomer because, although they may yield the same decomposition products, the relative amounts may be different. In a few cases, especially for stereoisomers, the spectra of two compounds may be so nearly identical that separate determination is impossible. Then the two substances must be lumped together.

Applications. Mixtures of nearly all materials exerting a vapor pressure greater than about 0.2 mm. of Hg at room temperature may be analyzed. For exacting quantitative work, it is necessary that a pure sample of each component to be determined be available for calibration of the instrument. For most qualitative work, however, this is not a rigid requirement as it is frequently possible to predict the approximate spectrum of a substance from knowledge of the spectra of related materials.

With the Consolidated Mass Spectrometer the entire mass range from hydrogen, mass 2, to mass 150 may be scanned, if desired. This may be accomplished by using one magnetic field strength adjustment for hydrogen, a second for the range of masses of 12 to 100, and a third for the range of 100 to 150. If more desirable, the single range of mass 18 to 150 may be scanned without adjustment of the magnet current.

In the upper range, with normal adjustment of the accelerating slits, mass 150 can be resolved from mass 151, and in the lower ranges even one-quarter mass units are separable. Without appreciable sacrifice of instrument sensitivity, special adjustment of the exit slit can be made which will increase the resolving power to such a degree that masses in the range of 300 can be separated.

The speed of automatic scanning of one octave of mass numbers, that is, mass 60 to 120, is about 2 minutes. If it is desired to rescan a single peak several times for increased accuracy or for kinetic studies, this can be done manually at the rate of about 6 to 10 scans per minute.

Mixtures containing up to as many as twenty components can be analyzed, and quantities of material as low as 0.1% can be determined in complicated hydrocarbon mixtures. Only very small gas samples, 0.1 to 0.2 ml. of material, are needed.

Absolute accuracy in the quantitative determination of any element or compound depends on its concentration in the mixture, on the presence of other materials contributing to its spectrum, on its sensitivity to electron bombardment, and on certain external physical factors. No general statement concerning precision can therefore be made. However, deviations are usually within the range of 0.05 to 1.0 mole per cent, and usually are comparable to, or less than, that which can be expected from other methods of analysis.

The length of time required to make analyses, including calculations, is short, only about 2.5 man-hours for petroleum samples as compared which 10 days, 24 hours a day, for comparable analyses using fractionating columns. If it is not desired to check for unexpected compounds and general accuracy of analyses, or if it is desired to use the spectrometer for control purposes only, the time required for each analysis may be materially shortened. Calculation time may also be materially shortened by employing electrical computers.

Virtually every hydrocarbon in the range C_1 to C_9 of interest in research or manufacturing in the petroleum industry can be quantitatively determined, provided that pure materials are available for calibration purposes. In the higher molecular weight ranges, analyses become increasingly difficult due to the large number of possible isomers; but, unless detailed information is required, computations can be greatly simplified by grouping substances, that is, "total C_6 paraffins," "total C_7 olefins," etc.

Pretreatment of the sample by means of rough fractionations is sometimes required of complex refinery mixtures. In general, a sample containing petroleum hydrocarbons ranging from C_1 through C_5, plus several mole per cent of C_6 and inorganic gases, can be analyzed directly. If heavier substances are present, a rough fractionation is necessary. Above the C_5 range, samples can be analyzed directly if they contain ten or fewer components.

The spectra of the oxygenated compounds such as ethers, esters, aldehydes, ketones, acids, thio-aldehydes, etc., are sufficiently distinctive that good accuracy can be expected in determinations of their mixtures. A multitude of other types of compounds - sulfides, chlorides, fluorides, iodides, mercaptans, amines, nitroparaffins, terpenes, etc. - can be determined, either when present as impurities or as the major constituents.

Water vapor and alcohols, being highly polar compounds, tend to be absorbed on the metal and glass surfaces of the apparatus and, therefore, cannot be accurately determined by normal procedures. Special techniques have sometimes resulted in acceptable determinations. Strong oxidants can be determined, but care must be taken to prevent prolonged contact in the instrument because of the danger of damage to the apparatus.

Stable isotopes are widely used to "tag" compounds and thus serve as tracers to determine the ultimate fate of the compounds in chemical or biological reactions. Only a limited number of stable isotopes in sufficiently concentrated form are available, however. Practically all of these are isotopes of the lighter elements, H, B, C, N, O, S, and Cl. Deuterium can be obtained commercially in 99.9% purity and N^{15} in 60% purity. Other isotopes are becoming available due to the development of mass spectrographic and thermal diffusion procedures of separation for the atomic energy project. Prior to the advent of the mass spectrometer, the chief methods for the determination of the concentration of isotopes were (1) density measurements, (2) refractive index, (3) thermal conductivity, (4) isotopic effects in spectra, and (5) chemical atomic weight determinations.

The isotope dilution method, previously described in Chapter VII for radioactive isotopes, can be employed here to determine the amount of a substance present in a complex mixture. It is only necessary to know the ratio of isotopes present in the added sample of the substance, the ratio present in the final sample isolated from the mixture, and the weight of the added sample. It is not necessary that the substance being determined be quantitatively separated from the mixture; only a few milligrams of pure substance are necessary. Rittenberg and Foster[4] have applied this method to the analysis of complex mixtures of amino acids.

The mechanism of the Arndt-Eistert reaction has been elucidated by Huggett and co-workers[5] using C^{13}. Similarly, C^{13} and O^{18} have aided Ruben and co-workers[6] in their study of photosynthesis.

A less expensive adaptation of the usual mass spectrometer, the isotope-ratio mass spectrometer, Fig. X-6, is available for work in these

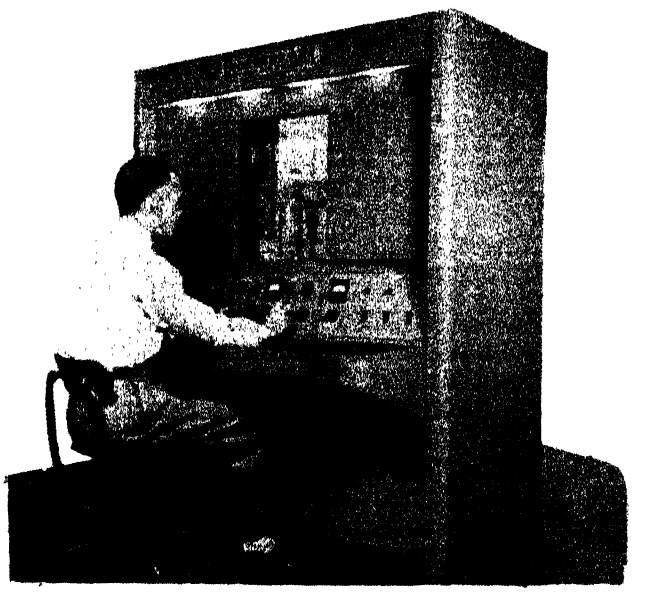


Fig. X-6. The Consolidated-Nier Isotope-Ratio Mass Spectrometer, Model 21-201 (Courtesy of Consolidated Engineering Corporation)

4. Rittenberg, D. and Foster, G. L., J. Biol. Chem. 133, 737 (1940).

5. Huggett, C., et. al., J. Am. Chem. Soc., 64, 3043 (1942).

6. Ruben, S., et. al., ibid., 63, 877 (1941).

fields. In the modified instrument the ion currents from two ion beams, for example, the ion beams from carbon^{13} dioxide and carbon^{12} dioxide, are collected simultaneously by means of a double exit slit and amplified simultaneously by two separate amplifiers. The larger of the two amplified currents is then attenuated with a set of decade resistors by the operator, until it will exactly balance the smaller current from the amplifier. The ratio of the two currents is determined from the resistance required. This is a null method and practically eliminates the effect of other variables in the system. Reproducibilities of better than 1% are claimed for this instrument. Thus the device is valuable for detecting a tracer material even after great dilution.

Another special application of the mass spectrometer is in the determination of the kinetics of reactions.[7] The time required to record the peak heights is so small, especially if only one peak is being scanned, that changes during an actual determination are not large if the reaction rate is moderate. This method of following a reaction is especially useful when only small amounts of substances are present, and it is possible to detect the presence of intermediates or even of free radicals.

The mass spectrometer can be used to determine ionization potentials of molecules. The ionizing electron beam is increased in energy gradually until the desired ion peak is noted in the spectrum.

One of the major analytical problems in chemical industries is the detection of small amounts of impurities. It is possible to detect as little as 0.003% diethylbenzene in ethylbenzene. As little as 0.001% of oxygen in nitrogen can be determined routinely in annealing furnace atmospheres.[8]

The mass spectrometer is an extremely sensitive device for detecting leaks in systems. Cheap, compact, portable instruments, Fig. X-7, designed especially for such work are capable of detecting as little as 1 part of helium in 400,000 parts of air. A leak can be detected which would allow the passage of 1 ml. of helium in 16 years. In use, the system under test is evacuated and a continuous sample of gas from it is pumped through a throttle valve into the leak detector. A small jet of helium is directed at the area suspected of leaking. When helium from the probe jet passes through a leak into the system, the increased ion current, or an audible signal device, permits location of the leak to within 1/32 inch.

Fig. X-7. Portable Mass Spectrometer Leak Detector. Detector protects vacuum systems (Courtesy of Westinghouse Electric Corporation)

7. Leifer, E., and Urey, H. C., ibid., 64, 994 (1942).

8. Hipple, J. A., J. Applied Phys., 13, 551 (1942).

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1. Hipple, J. A., J. Applied Phys., 13, 551 (1942).
2. Symposium on the Mass Spectrometer as an Industrial Tool, J. Applied Phys., 13, 525 et seq. (1942).
3. Smyth, H. D., Rev. Modern Phys., 3, 347 (1931).
4. Washburn, H. W., Riley, H. F. and Rock, S. M., Ind. Eng. Chem., Anal. Ed., 15, 541 (1943); ibid., 17, 74 (1945).
5. Weissberger, A. (Ed.), "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, Vol. II, pp. 1291-1341.

CHAPTER XI

THE CENTRIFUGE

The purpose of the centrifuge is to increase the force of gravity and thereby to accelerate the separation of two phases. It may be used to separate solids from gases, for example, dust or fine spray from air, as in the automobile air cleaner; but in the laboratory it is used to separate a solid from a liquid or two immiscible liquids from each other.

The force developed by the centrifuge is expressed by the formula $\frac{4N^2\pi^2r}{g}$, where N = revolutions per second, r = radius, g = 980.6. If r = 15 cm. and N = 80 or 480 r.p.m., the force developed is nearly 4000 times gravity. In the so-called supercentrifuges which develop an enormous force, the radius is small but the speed is very high.

The use of the centrifuge in analytical work may be divided into (a) the separation and washing of precipitates (replacing filtration); (b) the determination of the amount of a precipitate by measuring its apparent volume when packed into a graduated tube; (c) the determination of a substance by measuring the volume of an immiscible liquid, for example, butterfat in milk; (d) removal of mother liquor from crystals to increase the efficiency of purification by recrystallization.

The Washing of Precipitates.[1] The advantages of centrifugal washing of precipitates as compared with filtration are: (1) It is more rapid in the case of gelatinous or very fine-grained precipitates which tend to clog the filter paper; (2) the separation from the mother liquor is more complete; (3) the precipitate may be completely stirred up with the wash solution each time; (4) it can be used in cases where filtration is impossible.

Determination by Measuring the Apparent Volume of a Precipitate. The precipitate obtained in the usual way, together with the mother liquor, is washed into centrifugal tubes, the lower portion or stem of which is graduated. The precipitate is caused to settle into the stem as much as possible and is then centrifuged until it attains a constant height. The column is read and reduced to the weight standard by comparison with a precipitate similarly obtained from a known weight of the substances.

The method has been applied by Arrhenius[2] to precipitates of potassium chloroplatinate, potassium cobaltinitrite, barium sulfate, "nitron" nitrate, calcium oxalate, ammonium molybdiphosphate, and magnesium ammonium phosphate. Good results were obtained. The maximum error with barium sulfate was 0.2 mg. on 15 mg. of sulfate; with calcium oxalate, 0.01 mg. on 1.4 mg.; with ammonium molybdiphosphate, 0.003 mg. phosphate on 0.23 mg.

Gotz first used this method for the determination of phosphorus in steel. It was described by Wedding[3] and elaborated by Bormann.[4] The precipitate of ammonium molybdiphosphate was formed in the usual way and centrifuged for 2 minutes at 1200 r.p.m. Using 1.2 g. of steel, the divisions on the tube, divided by 2, show hundredths of 1% of phosphorus. The deviation from the gravimetric method was $\pm$ 0.005% phosphorus, and the whole determination required 30 minutes.

A more detailed study of the method was made by Green[5] using barium sulfate. He found that the apparent density increased as the weight of the precipitate increased from 2.5 with 6 mg. to 2.8 with 55 mg. The coarser the particles, the greater the apparent density; therefore conditions favoring the formation of larger particles will give a higher apparent density. Using 30.6 mg. of barium sulfate in all experiments, he obtained the results which are shown on the following page. His conclusions were: (1) Any condition of precipitation which affects the physical properties of the precipitated particles will affect the volume of such particles when packed into capillary tubes by centrifugal force; (2) for accurate work it is only necessary to calibrate a tube under definite conditions by the use of standard samples and to use this tube under those conditions for all subsequent determinations; (3) the conditions may be selected at will so long as these conditions are followed in all determinations; (4) for volumes above the midpoint of the capillary, results with identical

1. Parker, H. G., J. Am. Chem. Soc. 31, 549 (1909).

2. Arrhenius, O., J. Am. Chem. Soc., 44, 132 (1922).

3. Wedding, Stahl u. Eisen, 7, 118 (1887).

4. Bormann, K., Z. angew, Chemie., 2, 638 (1889).

5. Greene, H. S., J. Am. Chem. Soc., 53, 3275 (1931).

Temperature of Precipitation	Apparent Density	Precipitant	Apparent Density
26°	1.54	H_2SO_4	2.61
60°	2.16	Na_2SO_4	2.37
80°	2.37	$MgSO_4$	2.25
100°	2.62		
Rate of Adding H_2SO_4 Drops per Min.		Time of Standing at 90°, Hrs.	
10	2.63	0	2.60
30	2.58	6	2.65
70	2.27	24	2.74
Concentration of $BaCl_2$ Solution		Rate of Centrifuging, r.p.m.	
0.025N	2.35	800	1.87
0.01	2.47	1600	2.50
0.002	2.61	2000	2.56
		Time of Centrifuging, Min.	
		1	2.18
		3	2.52
		4	2.57

samples under identical conditions may be checked with an error of less than 1%.

With hydrous aluminum oxide 1 ml. of precipitate contained about 5 mg. of aluminum, so that differences of 0.1 mg. could be measured. Centrifugal methods are often used where rapidity is essential and only a fair degree of precision is demanded, as, for example, in the determination of sulfate in chromic acid plating baths.

Determination by Measuring the Volume of an Immiscible Liquid. H. Copaux[6] has devised a method for phosphorus based upon a measurement of the volume of the ether compound of molybdiphosphoric acid. If to an acid solution of phosphoric acid and ether, sodium molybdate is added and the liquid shaken, three layers form, the lowest yellow one containing the molybdiphosphoric acid ether compound,

$$2(H_3PO_4 \cdot 12MoO_3) \cdot 99H_2O + 37(C_2H_5)_2O.$$

The composition is approximately constant, and 1 mg. P_2O_5 yields 0.05 ml. of liquid.

Poussigues[7] has applied a similar method to the determination of arsenic in the form of arsenic acid. Sodium molybdate, acidified with nitric acid, is mixed with ether and treated with

6. Copaux, H., Comp. rend., 173, 656 (1921).

7. Poussigues, M., Ann. Chim. anal. chim. appl., 5, 265 (1923).

arsenic acid as in the Copaux method for phosphorus. The bottom layer is the ether compound of molybdiarsenic acid. After centrifuging, the volume of the ether compound is measured and compared with a standard. If no phosphorus is present, the method is accurate, but a correction must be applied for the solubility of the liquid in the water solution.

Use of the Centrifuge in Purifying Materials. After recrystallizing a salt it is customary to suck the crystals dry on filter paper or to press them between filter papers. In very careful work this is not permissible, because fibers of paper get in. Also, it is not very efficient in removing mother liquor. Richards[8] of Harvard has determined quantitatively the advantages of centrifugal drainage - used so much in technical processes and so little in laboratory work. Sodium nitrate was chosen because it does not crystallize in plates or needles, and nitric acid was chosen as the impurity.

Four hundred and fifty grams of sodium nitrate were dissolved in 220 g. of water and 15 g. of concentrated nitric acid added; this is a solution containing about 2% of impurity. Two hundred and forty grams of sodium nitrate crystallized out and the resulting mother liquor was about 0.5 N in acid. After merely draining, 10 g. of crystals retained 3.5-4 g. of mother liquor, or about 0.1 g. of nitric acid, which is 1% impurity. Suction removed half of this, leaving 0.5% impurity. The crystals were then centrifuged in a porcelain basket having a radius of 65 mm. and a speed of 2000 r.p.m. After 2 minutes two thirds of the liquor was removed, and washing with 25 ml. of water while rotating removed two thirds of the remainder. Ten grams of crystals now contained only 0.005 g. of nitric acid or 0.05%, equal to 1/20 of the amount removed by drainage. The crystals remaining were then washed again with a little water, dissolved in the least possible amount of boiling water, and recrystallized. The mother liquor was only 1/300 N in nitric acid or 150 times as dilute as the original mother liquor. After centrifuging 2 minutes, 10 g. of crystals retained 0.5 ml. of liquor, corresponding to 0.1 mg. of nitric acid in 10 g. of salt, an impurity of 0.0001% or 1 part in a million, which was not at all easy to detect. Thus two crystallizations with centrifucal drainage and washing removed 99.995% of the impurity.

Let us compare this with drainage by gravitation alone. Two recrystallizations removed 0.9 of the impurity; nine would have been required to attain what was accomplished by two with centrifugal drainage, and only about 2 g. of sodium nitrate would have remained from 1000 g. originally taken, whereas 184 g. would have been the yield after two centrifugal treatments. The salt obtained centrifugally would be 2000 times as pure as that obtained by gravitational draining, and to attain an equal degree of purity the yield is 100 times as great by the centrifugal process, and much time and labor are saved. When the salt forms plates or needles, the advantage of centrifugal drainage is greater. With $Na_2CrO_4.4H_2O$ it was twice as great. The results with one batch of sodium nitrate and the following successive treatments are summarized in the following table:

Treatment	Mother Liquor per 10 g. salt g.	Impurity %
Drainage	3.5	1.0
Suction	1.6	0.5
Centrifuge	0.5	0.16
Washing		0.05
More Washing and Crystallization	0.5	0.001
More Washing		0.0001

Efficiency of Centrifugal Washing. Two hundred grams of crystals were sprayed with 200 ml. of water. The efficiency progressed until 150 ml. were used. Forty per cent of the salt dissolved and the washings contained 0.01 as much acid as the mother liquor. Further washing had little effect.

The 60% left contained only 1% of the impurity that would have adhered without centrifugal washing; the process is, therefore, very advantageous, but it has two disadvantages - the danger of uneven spraying and the possibility that the liquor in the interstices between crystals may not be touched. It is more efficient to mix the crystals with water. Two hundred and fifty grams of crystals were mixed with 57 ml. of N nitric acid and the 200 g. remaining were whirled, stirred into 45 ml. of water, whirled, stirred into 30 ml. of water, whirled, stirred into

8. Richards, T. W., J. Am. Chem. Soc., 27, 104 (1905).

25 ml., and again whirled. The 110 g. remaining contained hardly a trace of acid, whereas the mother liquors were 0.06 N, 0.006 N, and 0.0004 N respectively. Using the same amount of water by continuous spraying gave better yields, but left 50 times as much impurity. How long to wash depends on the solubility of the salt and on various other factors. In most cases it is sufficient to wash twice with enough water to make the mass pasty. The reason for the efficiency of centrifugal washing is that so much of the preceding impure solution is removed that the new portion of water dilutes the impurity enormously.

It is obvious that when the composition of the crystals is almost the same as that of the mother liquor, as in the separation of the rare earths, there is no advantage in centrifugal drainage.

LABORATORY WORK WITH THE CENTRIFUGE

1. Determination of Phosphate by the Copaux Method. Reagents: Sulfuric acid, 100 g. per liter. Sodium molybdate prepared as follows: Add 100 g. of molybdic oxide to about 500 or 600 ml. of water, add to the warm mixture about 35 g. of sodium carbonate; and, when the oxide has dissolved as far as possible, add more sodium carbonate in small portions to the warm solution until the oxide just dissolves, avoiding any considerable excess. Dilute the solution to 1 liter.

Procedure. Into a tube with a capacity of 60 ml., the lower portion of which is about 80 mm. long and 6 mm. in diameter, graduated to 0.1 ml., place 10 ml. of phosphate solution containing about 10 to 25 mg. of phosphorus pentoxide, 10 ml. of the dilute sulfuric acid, cover 3-4 mm. deep with ether, and shake. Then add 15 ml. of sodium molybdate in five or six portions, shaking after each addition. Citric acid must be absent.

To a second tube add a known phosphate solution and treat as above. Carefully balance the tubes to avoid vibration. Centrifuge the two solutions 4 minutes and compare the volumes of the heavy ether addition compound in both tubes. The relative volumes of the two liquids are proportional to the amounts of phosphorus. Construct a calibration curve from at least three standards. Calculate the amount of phosphorus in the unknown and report the data to the instructor. Total volume of aqueous solution must always be the same; balance tubes with ether.

2. Babcock Method for Fat in Milk. Stir the milk thoroughly, and measure 17.6 ml. from a special pipet into a clean Babcock bottle. To this add just an equal volume of sulfuric acid (sp. gr. 1.82). If too concentrated acid is used, charring will result; if the acid is too dilute, all the casein will not be dissolved. Mix the contents of the bottle thoroughly and, when solution is complete, place the two balanced bottles on opposite sides of the centrifuge shaft. Run the centrifuge 4 minutes. Add boiling water to each bottle until its surface is just below the neck and centrifuge 1 minute. Add sufficient boiling water to bring the fat into the graduated portion of the neck and centrifuge for 1 minute. Bring the fat to temperature by submerging the neck of the bottle for a short time in water at 60°C. Read the bottom of each meniscus and the difference is the percentage of fat. The tube is graduated to read in per cent and tenths of 1%.

3. Determination of the Apparent Volume of a Precipitate. The centrifugal tubes for this purpose are about 25 or 30 mm. in diameter at the top and are provided with a steep funnel below, leading to a graduated capillary tube about 40 mm. long and, for compact and dense precipitates, about 1 mm. in bore. For voluminous precipitates the bore may be as large as 10 mm. A list of suitable precipitates has already been mentioned.

Transfer the precipitate obtained in the usual way, together with the mother liquor into the centrifugal tubes. Cause the precipitate to settle into the stem as much as possible, and centrifuge it until it attains a constant height. This will usually require not more than 30 minutes at 2000 r.p.m. Prepare and precipitate in exactly the same way two more standards and centrifuge the two tubes for 4 minutes, at the same time taking care that the tubes are balanced to avoid vibration. Read the apparent volumes of the two precipitates; construct a calibration curve using the values obtained from the three standards, and calculate the amount of substance in the unknown. Report to the instructor the weight of the substance in the unknown together with all data.

To remove the precipitate from the capillary tube it will probably be necessary to use a thin stiff wire followed by flushing with a narrow tube. Applying suction through a thin tube is often helpful.

CHAPTER XII

DETERMINATION OF THE pH OF A SOLUTION

Acid-Base Equilibria

Acids and Bases. The most fundamental definition of an acid, an electron pair acceptor, and of a base, an electron pair donor, was enunciated by G. N. Lewis. Perhaps more practical definitions, although somewhat limited in application, are those due to Brönsted and Lowry, who defined an acid as any substance having a tendency to split off protons; whereas one which has the property of combining with protons to form an acid is called a base. Therefore, an acid always forms a conjugated system with a base:

$$\text{Acid} \rightleftharpoons \text{Base} + \text{Proton} \qquad (1)$$

Acids or bases may be either neutral molecules or positive or negative ions:

Acid	Base	Proton
HCl	$\rightleftharpoons Cl^-$	$+ H^+$
NH_4^+	$\rightleftharpoons NH_3$	$+ H^+$
$H_2PO_4^-$	$\rightleftharpoons HPO_4^{--}$	$+ H^+$
$Al(H_2O)_6^{+++}$	$\rightleftharpoons Al(H_2O)_5(OH)^{++}$	$+ H^+$

It has been found that a measurable ionization of an acid or base occurs only when the solvent can either combine with the protons derived from the acid or supply protons to combine with the base. If the solvent has no acid or basic properties, dissolved acids and bases will be present completely in the nonionized form. Fortunately, our commonest solvent, water, has both acidic and basic properties; in other words, it is amphiprotic or amphoteric since

$$H_2O \rightleftharpoons OH^- + H^+ \qquad (2)$$

and

$$H_2O + H^+ \rightleftharpoons H_3O^+ \qquad (3)$$

By the summation of equations (2) and (3) the equation for the ionization, or protolysis, of water is obtained:

$$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+ \qquad (4)$$

Alcohols and other polar type solvents will exhibit similar amphiprotic behavior, and will give rise to difficulties when they are present in aqueous solutions.

The mass action expression for the water equilibrium (4) may be formulated:

$$\frac{[H_3O^+]\,[OH^-]}{[H_2O]^2} = K, \text{ at constant temperature.} \qquad (5)$$

In any dilute aqueous solution the concentration of non-ionized water is very large, approximately 55.5 molar, and substantially constant. Hence

$$[H_3O^+]\,[OH^-] = [H_2O]^2 K = K_W \qquad (6)$$

This constant is called the ion product constant of water and has the following values at various temperatures:

$K = 1.2 \times 10^{-15}$ at 0° C.
$= 1.0 \times 10^{-14}$ at 25° C.
$= 5.8 \times 10^{-13}$ at 100° C.

In pure water the hydrogen-ion and the hydroxyl-ion concentrations are equal; at 25° C. each has a value of 1.0×10^{-7} molar.

pH Values. For purposes of brevity and convenience as well as for theoretical reasons, Sørenson[1] proposed that the negative common logarithm of the molar hydrogen-ion concentration be defined as pH:

$$pH = -\log[H^+] \qquad (7)$$

The pH of an acid solution is less than 7; that of an alkaline solution is greater than 7. pH is then the actual acidity and alkalinity of solutions as contrasted with the total or titratable acidity and alkalinity.

However, the pH system suffers from one disadvantage. It is obvious to anyone that a hydrogen-ion concentration of 4×10^{-5} is twice that of 2×10^{-5}; yet, it is not at all obvious when the respective pH values are stated as 4.40 and 4.70.

The Activity Factor. The expressions which we have been using heretofore for the various equilibrium reactions are incorrect from the standpoint of thermodynamics. Strictly speaking the ionization constant expression for the dissociation of a slightly ionized acid should be written:

1. Sørenson, S.P.L., Compt. rend. Lab. Carlsberg, 8, 1 (1909).

$$\frac{a_{H^+} \cdot a_{A^-}}{a_{HA}} = K_{ion} \qquad (8)$$

where the symbol a represents the activity of the component involved. It is well known that in calculations involving electrolytes in solution, the apparent concentration, or degree of ionization, approaches 100% only as the dilution approaches infinity. The reasons for this phenomenon are embodied in the Debye-Hückel Theory. This necessitates determining the activity of an ion or molecule by multiplying the respective molar concentration c by an activity coefficient f:

$$a = f \cdot c \qquad (9)$$

The activity coefficient of each component varies, however, with the ionic strength of the solution, and is equal to unity only in infinitely dilute solutions. At finite concentrations, the value of the coefficient is dependent upon the amount and type of the other ions present in the solution. Lewis and Randall suggested that the activity coefficient of a component is the same in all solutions of the same ionic strength, a term which may be defined as one half the sums of the product of each component concentration in the solution multiplied by the square of its valence z:

$$u = \frac{c_1 z_1^2 + c_2 z_2^2 + \cdots\cdots\cdots}{2} \qquad (10)$$

Consequently, rewriting and rearranging equation (8), we find,

$$paH = pK_{ion} - \log \frac{f_0[HA]}{f_1[A^-]} = pK + \log f_1 - \log \frac{[HA]}{[A^-]} \qquad (11)$$

since f_0 is nearly equal to unity for slightly ionized materials. In many subsequent equilibria the added refinement of activity coefficients will not be included. Often the coefficients will not be known. Sometimes the two coefficients are approximately equal and thereby cancel.

Buffer Action. If, to 1 liter of water, pH = 7, we add 1 ml. of 0.01 N hydrochloric acid, the solution will have a pH of 5. If we add this same amount of acid to a mixture of a weak acid and its salt, the change will scarcely be noticeable. Buffer action then can be defined as the resistance exhibited by a solution to change in pH through addition of acid or alkali, or upon dilution with further solvent.

By referring to a titration curve for acetic acid or any other weak acid it will be noted that, although the rate of change of pH at first is rapid, it becomes very slow after considerable acetate has been formed and again becomes rapid when most of the acid has been neutralized. The buffer effect is noticeable, therefore, only when both acid and salt are present. A mixture of a single weak acid and its salt will tend to stabilize the solution only within narrow pH limits. The pH at the middle point of the effective zone is determined approximately by the value of pK for the acid or base concerned, as can be shown by rearranging the expression for the ionization of a moderately weak acid,

$$\frac{[H_3O^+][A^-]}{[HA]} = K_a \qquad (12)$$

and taking the negative common logarithm,

$$pH = pK_a + \log \frac{[salt]}{[acid]} \qquad (13)$$

so that, if the concentrations of salt and undissociated acid present are equal,

$$pH = pK_a \qquad (14)$$

A distinction should be made between the pH level at which a buffer operates, and the capacity of the buffer to absorb or offset changes in pH. The level at which a buffer operates is determined by the ionization constant of the weak acid or base that is used, and the ratio of concentrations of acid and its salt, or base and its salt, respectively. The common ion effect is the important factor in maintaining the pH at a given level. A maximum buffer action is observed in a mixture with equal concentrations of salt and acid, and it decreases with increasing or decreasing ratio of salt to acid. The buffer capacity also depends upon the total concentration of the buffer mixture. For example, it would take ten times as much acid or base to change by one unit the pH of a mixture molar in both acetic acid and sodium acetate as would be required to produce a change of one pH unit in a mixture that is tenth molar in these substances. Buffer action may depend also upon the nature of the substances added. Presence of a weak acid usually shows more buffer effect than the presence of a strong acid. If any substance absorbs any of the constituents which affect pH, it will act as a buffer. Maintenance of neutrality by solids such as calcium carbonate, zinc oxide, etc., may be considered a buffer action.

Buffer solutions are of the utmost importance in the measurement of the hydrogen-ion concentration and in many other aspects of chemical

TABLE 1. BUFFER SOLUTIONS OF CLARK AND LUBS (20°)

0.2 N HCl with 0.2 N KCl (14.92 g. KCl per Liter)

pH	Composition (per 200 c.c. Solution)
1.0	97.0 c.c. HCl + 50 c.c. KCl
1.2	64.5 c.c. HCl + 50 c.c. KCl
1.4	41.5 c.c. HCl + 50 c.c. KCl
1.6	26.3 c.c. HCl + 50 c.c. KCl
1.8	16.6 c.c. HCl + 50 c.c. KCl
2.0	10.6 c.c. HCl + 50 c.c. KCl
2.2	6.7 c.c. HCl + 50 c.c. KCl

0.2 N HCl with 0.2 Molar Potassium Biphthalate (40.84 g. per liter)

pH	Composition (per 200 c.c. Solution)
2.2	46.70 c.c. HCl + 50 c.c. Biphthalate
2.4	39.60 c.c. HCl + 50 c.c. Biphthalate
2.6	32.95 c.c. HCl + 50 c.c. Biphthalate
2.8	26.42 c.c. HCl + 50 c.c. Biphthalate
3.0	20.32 c.c. HCl + 50 c.c. Biphthalate
3.2	14.70 c.c. HCl + 50 c.c. Biphthalate
3.4	9.90 c.c. HCl + 50 c.c. Biphthalate
3.6	5.97 c.c. HCl + 50 c.c. Biphthalate
3.8	2.63 c.c. HCl + 50 c.c. Biphthalate

0.2 N NaOH with 0.2 Molar Potassium Biphthalate (40.84 g. per Liter)

pH	Composition (per 200 c.c. Solution)
4.0	0.40 c.c. NaOH + 50 c.c. Biphthalate
4.2	3.70 c.c. NaOH + 50 c.c. Biphthalate
4.4	7.50 c.c. NaOH + 50 c.c. Biphthalate
4.6	12.50 c.c. NaOH + 50 c.c. Biphthalate
4.8	17.70 c.c. NaOH + 50 c.c. Biphthalate
5.0	23.85 c.c. NaOH + 50 c.c. Biphthalate
5.2	29.95 c.c. NaOH + 50 c.c. Biphthalate
5.4	35.45 c.c. NaOH + 50 c.c. Biphthalate
5.6	39.85 c.c. NaOH + 50 c.c. Biphthalate
5.8	43.00 c.c. NaOH + 50 c.c. Biphthalate
6.0	45.45 c.c. NaOH + 50 c.c. Biphthalate

work. To make a buffer solution of a given pH, it is first necessary to choose an acid (or base) with a pK value as near as possible to the required pH (see equation (14)). The actual ratio of salt to acid necessary can then be found from equation (13). In practice, buffer solutions are generally used which have a buffer concentration between 0.05 and 0.10 N. These mixtures are effective approximately within a pH range:

$$pH = pK_a \pm 1 \qquad (15)$$

Standard Buffer Solutions. Buffer solutions constitute the basis of the greater part of colorimetric and some electrometric pH measurements. It is difficult to make an accurate pH determination in an unbuffered solution, as traces of carbon dioxide, or other acidic or basic substances, may easily change the pH. Many different types

TABLE 1 (cont'd)

0.2 N NaOH with 0.2 Molar Monopotassium Phosphate
(27.22 g per Liter)

pH	Composition (per 200 c.c. Solution)
6.0	5.70 c.c. NaOH + 50 c.c. Phosphate
6.2	8.60 c.c. NaOH + 50 c.c. Phosphate
6.4	12.60 c.c. NaOH + 50 c.c. Phosphate
6.6	17.80 c.c. NaOH + 50 c.c. Phosphate
6.8	23.45 c.c. NaOH + 50 c.c. Phosphate
7.0	29.63.c.c. NaOH + 50 c.c. Phosphate
7.2	35.00 c.c. NaOH + 50 c.c. Phosphate
7.4	39.50 c.c. NaOH + 50 c.c. Phosphate
7.6	42.80 c.c. NaOH + 50 c.c. Phosphate
7.8	45.20 c.c. NaOH + 50 c.c. Phosphate
8.0	46.80 c.c. NaOH + 50 c.c. Phosphate

0.2 N NaOH with 0.2 Molar Boric Acid in 0.2 Molar KCl
(12.37 g. Boric Acid and 14.91 g. KCl per Liter)

pH	Composition (per 200 c.c. Solution)
(7.8	2.61 c.c. NaOH + 50 c.c. Boric acid-KCl)
8.0	3.97 c.c. NaOH + 50 c.c. Boric acid-KCl
8.2	5.90 c.c. NaOH + 50 c.c. Boric acid-KCl
8.4	8.50 c.c. NaOH + 50 c.c. Boric acid-KCl
8.6	12.00 c.c. NaOH + 50 c.c. Boric acid-KCl
8.8	16.30 c.c. NaOH + 50 c.c. Boric acid-KCl
9.0	21.30 c.c. NaOH + 50 c.c. Boric acid-KCl
9.2	26.70 c.c. NaOH + 50 c.c. Boric acid-KCl
9.4	32.00 c.c. NaOH + 50 c.c. Boric acid-KCl
9.6	36.85 c.c. NaOH + 50 c.c. Boric acid-KCl
9.8	40.80 c.c. NaOH + 50 c.c. Boric acid-KCl
10.0	43.90 c.c. NaOH + 50 c.c. Boric acid-KCl

of buffer solutions have been proposed. However, the series proposed by Clark and Lubs[2] seems to be most popular, perhaps because the mixtures are stable and simple to prepare from materials easily obtained in pure form, and the equal intervals in pH values offer practical advantages. The various pH mixtures are made up from the following stock solutions: 0.2 M potassium chloride, 0.2 M potassium acid phthalate, 0.2 M mono-potassium dihydrogen phosphate, 0.2 M boric acid, 0.2 M hydrochloric acid, and 0.2 M sodium hydroxide. The amounts to be used for each particular pH value are given in Table 1 which is taken from Clark's book.[3] Potassium chloride is added to the boric acid solution to bring the ionic strength in the borate mixtures to a point comparable with that of the phosphate mixtures so that colorimetric checks may be obtained with the two series where they overlap. Mixtures of potassium chloride and hydrochloric acid are obviously not buffers, but are of constant ionic strength. They are used only for pH values between 1.2 and 2.2, such a solution being so acid that it need not be buffered.

A change in temperature affects the pH of these buffer solutions only slightly except in the case of

2. Clark, W. M. and Lubs, H. A., J. Bact., 2, 1, 109, 191 (1917).

3. Clark, W. M., "The Determination of Hydrogen Ions," 3rd Edition, Williams and Wilkins, Baltimore, 1928, pp. 200-201.

mixtures of boric acid and sodium hydroxide due to equilibrium shifts of the various polymolecular complexes of boric acid. In contrast buffers composed of weak bases and their salts are more sensitive to temperature changes, and for this reason buffer mixtures are usually composed of a weak acid and its salt.

It has been mentioned that the buffer range of a single acid and its salt is narrow. By combining several acids of varying strength with their salts, so-called "universal" buffer solutions are obtained which cover a wide range. One example is McIlvaine's buffer which employs a mixture of 0.2 M disodium hydrogen phosphate and 0.1 M citric acid. The citrate system functions between the two phosphate systems, thus the range pH 2.2 to 8.0 is covered. Other examples are given in Britton's book.[4]

Buffer tablets which cover most of the pH range are now commercially available. These tablets possess the advantage of eliminating the preparation, storage, and mixing of various solutions, it being necessary only to dissolve one tablet in a small volume of water to obtain the pH marked on the container.

The Bureau of Standards distributes a series of standard buffer salts or mixtures of salts.

Acid-Base Indicators. A practical pH colorimetric indicator must meet certain well-defined specifications: A definite, but gradual color change over a narrow pH range must be obtained, substances other than hydrogen or hydroxyl ions should not affect the color changes, and the color formation must occur rapidly and produce a stable color.

Theory of Indicators. Ostwald, in 1891, tried to show the relationship between the behavior of indicators and the theory of electrolytic ionization. He assumed that indicators are acids and bases, the non-ionized molecules of which have a color different from that of their ionized products. For each indicator there is a characteristic zone of hydrogen-ion concentration, on the acid side of which the indicator is completely transformed into its acid color and on the alkaline side of which it is completely transformed into its alkaline color. Within this range there will be different proportions of the acid and alkaline colors. If the non-ionized form of the indicator has acid properties, its ionization can be represented by the same equation and equilibria expression as that of all weak acids:

$$\underset{\text{acid color}}{HIn} + H_2O \rightleftharpoons H_3O^+ + \underset{\text{alkaline color}}{In^-} \quad (16)$$

and
$$\frac{[H_3O^+]\,[In^-]}{[HIn]} = K_{ion} \quad (17)$$

or
$$\frac{[In^-]}{[HIn]} = \frac{K_{ion}}{[H_3O^+]} \quad (18)$$

Therefore
$$pH = pK_{ion} + \log \frac{[In^-]}{[HIn]} \quad (19)$$

which is also
$$pH = pK + \log \frac{[\text{alkaline color}]}{[\text{acid color}]} \quad (20)$$

Ostwald's simple assumption, if unmodified, does not harmonize with what is now known. Researches into the phenomena of tautomerism have shown that when a change in color is observed in an indicator solution, the change is associated with the formation of a new substance which is generally a molecular rearrangement or "tautomer" of the old. But Noyes[5] showed that it is the degree of ionization, as determined by the hydrogen-ion concentration, that determines which tautomer predominates. Therefore, consideration of the tautomeric equilibria only modifies the original Ostwald equation to this extent: The true ionization constant is a function of the several equilibrium and ionization constants involving the different tautomers. These colors can be maintained with buffer solutions, the hydrogen-ion concentration of which remains constant; and, since they are characteristic at definite hydrogen-ion concentrations, they can be used to estimate this concentration by a system of comparison with standards.

Optical Aspects. It should not be forgotten that the phenomena observed in the color change of indicators are optical, and no theory is complete which fails to recognize this fact. Unfortunately, we have no adequate treatment of the subject which correlates in a practical manner electrolytic ionization, tautomerism, and the optical phenomena.

If we consider the range of an indicator as it is determined by the differentiating power of the human eye, it follows from equation (20) by differentiation that the maximum rate of increase in ionization is at the point where the alkaline color is equal to the acid color. But this is not the central point of the optical conditions for differentiating pH values because the eye has not

4. Britton, H.T.S., "Hydrogen Ions," I, Chapman and Hall, London, 1942, pp. 312-19.

5. Noyes, A. A., J. Am. Chem. Soc., 32, 815 (1910).

TABLE 2. LIST OF SATISFACTORY INDICATORS AND THEIR CONSTANTS

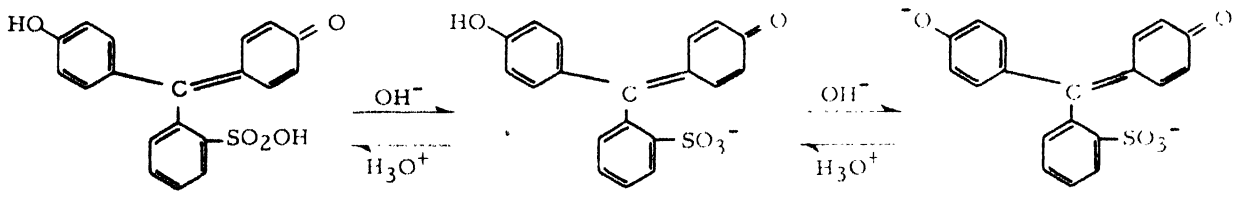
Indicator	pH Range	pK_{HIn}[a]	Abs. Max[b]	Color Change
Cresol Red (acid)	0.2 to 1.8			Red to Yellow
Thymol Blue (acid)	1.2 to 2.8	1.65	544 mμ	Red to Yellow
m-Cresol Purple	1.2 to 2.8	1.56	533[c]	Red to Yellow
Bromphenol Blue	3.0 to 4.6	4.10	592	Yellow to Blue
Bromcresol Green	3.8 to 5.4	4.66	617[c]	Yellow to Blue
*Methyl Red	4.4 to 6.3	5.00	530	Red to Yellow
Chlorphenol Red	4.8 to 6.4	6.05	573[c]	Yellow to Red
Bromcresol Purple	5.2 to 6.8	6.1	591	Yellow to Purple
Bromthymol Blue	6.0 to 7.6	7.1	617	Yellow to Blue
Phenol Red	6.4 to 8.2	7.8	558	Yellow to Red
Cresol Red (alk)	7.0 to 8.8	8.1	572	Yellow to Red
m-Cresol Purple (alk)	7.4 to 9.0	8.3	580[c]	Yellow to Purple
Thymol Blue (alk)	8.0 to 9.6	8.9	596	Yellow to Blue
*Phenolphthalein	8.0 to 10.0	9.7	553	Colorless to Red
*Thymolphthalein	9.3 to 10.5	9.9	598	Colorless to Blue
*Alizarine Yellow	10.0 to 12.0	11.1		Yellow to Violet

a. For an ionic strength of 0.1.
b. Absorption maxima for alkaline form from W. R. Brode, J. Am. Chem. Soc., 46, 585 (1924).
c. Cohen, B., Public Health Reports, 41, 3051 (1926).

only to detect differences, but also to resolve these differences from the color already present. Experience shows that the visual point of maximum rate of increase is near the limit of the useful range which lies on the side of lower color, except when there is no great difference in the command upon the attention by one color or the other, because the eye fixes instinctively upon the very dominant colors - red, blue, and purple.

Satisfactory Indicators. The number of indicators is very great. In his book, Clark[6] lists 185 which have been investigated, but many more are known. The indicators most used now are those of the sulfonephthalein series introduced by Clark and Lubs, and later extended by Cohen. These are brilliant in color, soluble in water, possess a sharp color change, and are most satisfactory in general. Table 2 lists the constants of this series. A few other indicators, preceded by an asterisk, are included to extend the range of the table.

Characteristics of the Sulfonephthaleins. The normal color change of the sulfonephthalein series may be represented by the following tautomeric equilibrium representing the structural changes for phenol red. The proportion of acid to alkaline form is determined by the second equilibrium. Some of the sulfonephthalein indicators - namely, thymol blue, cresol red, and m-cresol purple - exhibit two useful transformation



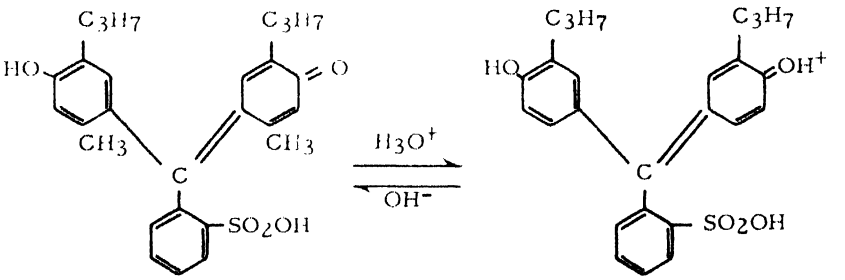
Quinoid form: Yellow

Acid form: Yellow

Quinone phenolate: Red

6. Clark, H. M., "The Determination of Hydrogen Ions," Williams & Wilkins, Baltimore, Md., 1928, pp. 76-90. See also Kolthoff, I. M., "Acid Base Indicators," The Macmillan Co., New York 1937.

regions: One in strongly acid medium from red to yellow, and the second from yellow to blue, red, or purple at pH values in the neighborhood of 7. Conflicting opinions prevail when explaining the changes in molecular configurations for the acid region. Kolthoff[7] has described it in the following manner, using thymol blue as an example:



Yellow Red

Absorption Spectra. Since the color exhibited by an indicator in solution is due to the selective absorption of certain frequencies of the incident light, Brode,[8] Cohen,[9] and Holmes[10] have studied the effect of changing hydrogen-ion concentration upon the absorption spectrum of various indicators. They found that no band shift occurred for most indicators, as regards wave-length, but merely changes in intensity of absorption. The wave-lengths of the absorption bands for certain indicators are included in Table 2. Fig. XII-1 shows typical spectrophotometric curves obtained by Brode.

Universal Indicators. Mixtures of several individual indicators, if properly chosen, will give different color tints over a wide range of pH. Several are on the market: One proposed by Bogen[11] contains these amounts of dyes: 100 mg. of phenolphthalein, 200 mg. of methyl red, 300 mg. of dimethyl-amino-azobenzene, 400 mg. of bromthymol blue, and 500 mg. thymol blue dissolved in 500 ml. of ethanol. Sufficient alkali is added to impart a yellow color. The color changes at various pH values are: Red, 2; orange, 4; yellow, 6; green, 8; and blue, 10. Accuracy of the different mixtures are not much more than 1 pH unit, but they are useful in the preliminary determination of pH.

Mixed Indicators. Small changes occurring at the normal transition point of an indicator can often be more easily detected by combining the indicator with a dye which possesses a color complementary to one of the indicator's colors, or by combining two indicators covering the same pH interval but showing contrasting colors. A well-known example is the mixture of methyl red and methylene blue which exhibits a dirty green at pH 5.6, dirty blue at 5.4, and red-violet at 5.2. Kolthoff[12] has tabulated many proposed combinations.

Fluorescent Indicators. When exposed to ultraviolet radiation the acid or alkaline forms of certain weak acids and bases exhibit a marked fluorescence. Before the advent of commercial glass electrodes, these substances provided one means for determining the pH of highly colored solutions. For example, beta-methylumbelliferone is useful over the pH range 5.8 (colorless) to 7.5 (blue fluorescence).

Indicator Papers. Indicator test papers are available which are compared with a color chart. By placing a drop of the test solution on the paper and noting the color developed, a very rough pH value of the material may be ascertained. For accuracy, however, such determinations are

7. Kolthoff, I. M., J. Phys. Chem., 35, 1433 (1931). See also Lund, H., Kgl. Danske Videnskab. Selskab., 11, No. 6. (1931).

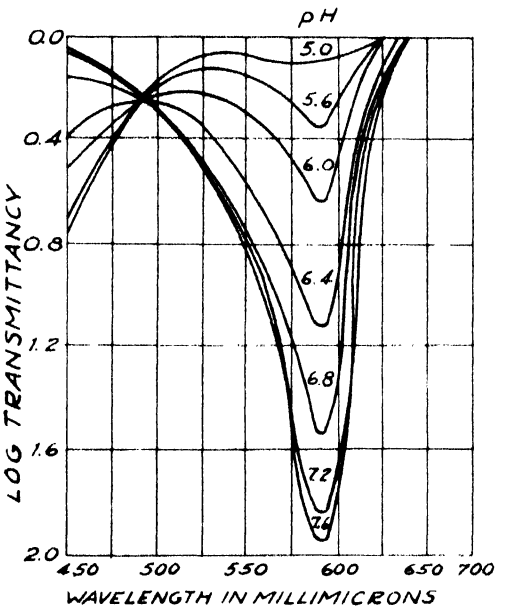
8. Brode, W. R., J. Am. Chem. Soc., 46, 581 (1924).

9. Cohen, B., Public Health Reports, 41, 3051 (1926).

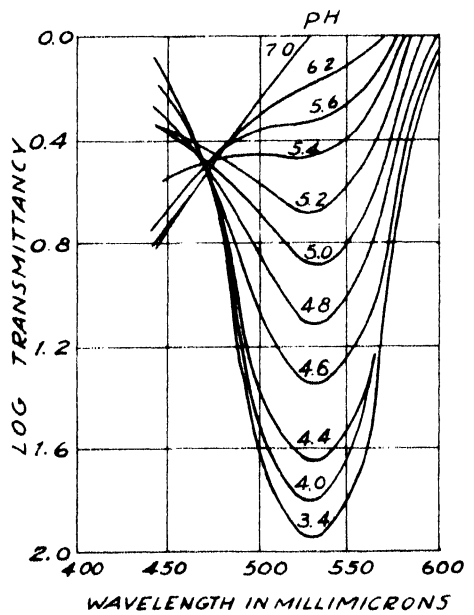
10. Holmes, W. C., J. Am. Chem. Soc., 46, 627; 47, 221, 226, 2232 (1925).

11. Bogen, E., J. Am. Med. Assoc., 89, 199 (1927).

12. Kolthoff, I. M., "Acid-Base Indicators," The Macmillan Co., New York, 1937, pp. 173-175.



(A) Bromcresol Purple



(B) Methyl Red

Fig. XII-1. Typical spectrophotometric curves of indicators (After Brode)

not at all comparable with the indicator solution method, because the shade of the spot produced may vary from the center outward making it difficult to determine which shade to consider as showing the actual pH. Papers also deteriorate rapidly.

pH Measurements. It has been pointed out already that the amount of actual ionized hydrogen-ions from acids, or hydroxyl ions from bases, is seldom equal to the total or titratable amount present in the solution. Even if the material were completely ionized, varying concentrations present in the solution or the presence of other substances capable of interaction would alter the concentration actually present from time to time. When certain salts are dissolved in water, not only does ionization occur but there is a tendency for them to react with the solvent, usually water, which acts as a weak acid or base (equations (2) and (5)) and thereby alter the pH. Take, for example, the salt BHA:

$$\underset{\text{base}_1}{BH^+} + \underset{\text{acid}_2}{A^-} + H_2O \rightarrow \underset{\text{acid}_1}{B^+} + \underset{\text{base}_2}{HA} + OH^- \qquad (21)$$

or

$$\underset{\text{acid}_1}{BH^+} + \underset{\text{base}_2}{A^-} + H_2O \rightarrow \underset{\text{base}_1}{BHOH} + \underset{\text{acid}_2}{H_3O^+} + A^- \qquad (22)$$

The general reaction is termed hydrolysis or protolysis, and salts subject to it are for practical purposes either acids or bases.

To determine the actual concentration of free hydrogen-ion in a solution we will now discuss the two general methods which enable us to make this determination in unknown materials. The potentiometric method depends upon measuring the potential produced when a given electrode is immersed in the solution to be tested. The colorimetric method depends upon the use of acid-base indicators which, as we have seen, possess the property of exhibiting different colors in solutions of varying pH.

Some of the factors which should be considered in a preliminary survey of suitable pH methods for industrial processes are the following, as pointed out by Perley:[13]

a. Is the solution of the highly buffered type or is it only sparingly buffered?
b. What is the solute composition and what variation in this composition will occur?
c. What is the temperature range of the process?
d. What is the pH range of the process?
e. How rapidly may the extreme changes of pH occur?
f. Are strong oxidizing agents present in the solution?
g. Will the process yield a colored solution, a colloidal suspension, turbidity, or a coarse mechanical suspension?
h. What variation in pH may be tolerated before adverse results are encountered in the process?

13. Perley, G. A., Trans. Am. Inst. Chem. Eng., 29, June (1933). Also, Chem. & Met. Eng., 40, 417 (1933).

i. Are any dissolved gases present in the solution?

At the present time no one method has been developed to cover all types of measurement. These next few sections will, therefore, present both the theory of each method of pH measurement and control, and the advantageous features and the limiting conditions of usefulness of these methods.

Colorimetric Detetermination of pH

Buffered Materials. If a suitable indicator is not known, one must be found which exhibits its intermediate color when added to a portion of the unknown. Next a series of buffer solutions are prepared with known pH values 0.2 pH unit apart that overlap the pH of the unknown. Then equal amounts of the correct indicator are added to equal volumes of these buffers and the unknown, all contained in test tubes possessing uniform diameter and thickness. Finally, a visual comparison is made of the color of the unknown with those of the known buffers against a white background until a color match is obtained or the unknown is judged to lie between two of the standard buffers. If precision greater than 0.1 pH unit is desired, additional standard buffers only 0.05 pH unit apart and lying between the previous two buffers could then be prepared and the color comparison process repeated. In no case should a color match with the first or last standard in any color standard set be taken as an accurate determination. In such cases the determination should be repeated with an indicator overlapping the former range.

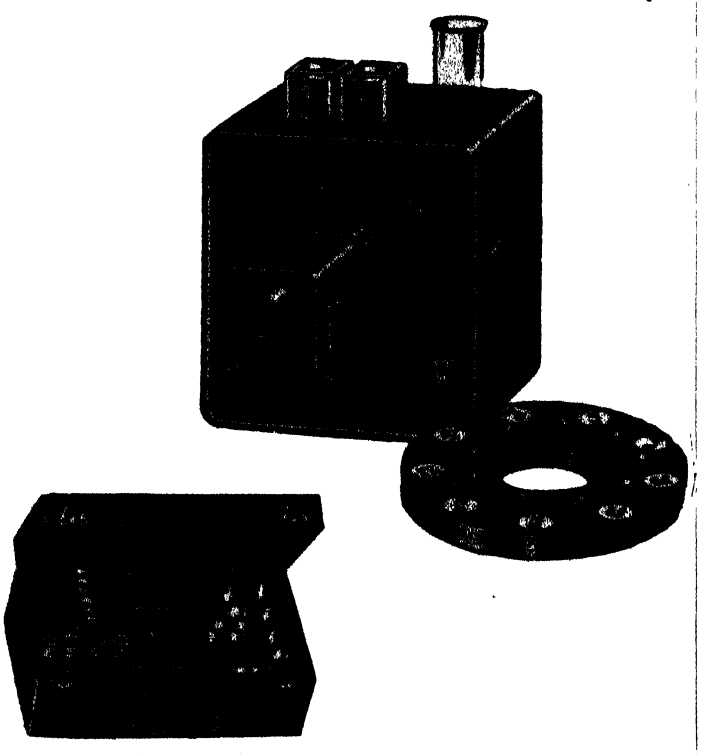
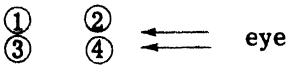


Fig. XII-2. The Hellige Comparator

Instead of preparing a series of standard buffer solutions containing the particular indicator, the color of the latter may be duplicated in glass or stained gelatin. The Hellige Comparator, Fig. XII-2 is supplied with a series of separate color discs reproducing various indicators which are viewed through a split field prism in juxtaposition with the unknown solution plus indicator. Each color disc consists of a number of colored glass standards, each one representing 0.2 pH unit, which can be revolved in the comparator.

Equation (20) tells us that if the pK of the indicator is known, the pH may be calculated if we determine the ratio of the alkaline color to that of the acid color. If the alkaline or ionized form is colored and the acid form colorless, the depth of color is a measure of the percantage of ionization. The full alkaline color (100% ionization) is compared colorimetrically with the solution containing the same concentration of indicator and intensity of color, and therefore the percentage of dissociation, will be inversely proportional to the depth of solution viewed when the colors are matched. This principle was used by Michaelis[14], who employed for this purpose as indicators various nitrophenols, phenolphthalein, and alizarine yellow GG. All these except phenolphthalein are yellow in alkaline solution and colorless in acid.

With two-color indicators, the procedure is not so simple. It becomes necessary to use Walpole's principle of the mixing of colors. Gillespie[15] devised a very simple method. Four test tubes of uniform size are placed so that one looks through each pair, thus:



In 1 is placed the acid form of the indicator, in 2 the alkaline form, the total number of drops of indicator in both tubes being always 10. Thus if 1 contains 3 drops, 2 must contain 7 drops. The volumes of solution must be the same - say, 10 ml. In tube 3 is placed 10 ml. of the unknown with 10 drops of indicator; in tube 4, 10 ml. of water. Tubes 1 and 2 are varied between a ratio of 1:9 and 9:1 until, looking through them, the color matches that of the unknown. This gives very simply and directly the ratio of dissociated

14. Michaelis, L. and co-workers, Biochem. Z., 109, 165 (1920); 119, 307 (1921).

15. Gillespie, L. J., J. Am. Chem. Soc., 42, 742 (1920); Soil Science, 9, 115 (1920).

to undissociated indicator, and equation (20) now becomes:

$$pH = pK + \log (\text{drop ratio}) \qquad (23)$$

in which the ratio is expressed as ratio of alkaline to acid color. A similar procedure could be used in Michaelis' method with one-color indicators.

Gillespie designed a special type of colorimeter for accomplishing this measurement more easily. (Fig. XII-3).

It consists of two vessels, C and E, two smaller ones, A and D, all fixed in position and having transparent bottoms. Another vessel, B, can be moved up and down between A and C and is attached to a scale. In C is placed the alkaline color and in B the acid color, each containing the same concentration of indicator. A and D are used only to compensate for color or turbidity. The unknown solution is placed in E, with the same concentration of indicator as in B and C. B is moved until the colors match. Equation (23) again would enable the final pH to be solved. If the unknown is colored or turbid, then tube A is filled with the test solution, and an equal quantity of distilled water is placed in D.

Unbuffered or Slightly Buffered Materials. Extraordinary precautions must be observed when measuring the pH of slightly buffered or non buffered materials. The introduction of slight impurities from the containers used or from the air may result in serious errors. Even the addition of the indicator dye, itself a weak acid or base, will produce errors in measuerment, and the proportion of unknown material and distilled water used in preparing the sample must be held constant if the results on different samples are to be comparable. It is often advisable to to use the isohydric method of Acree and Fawcett.[16]

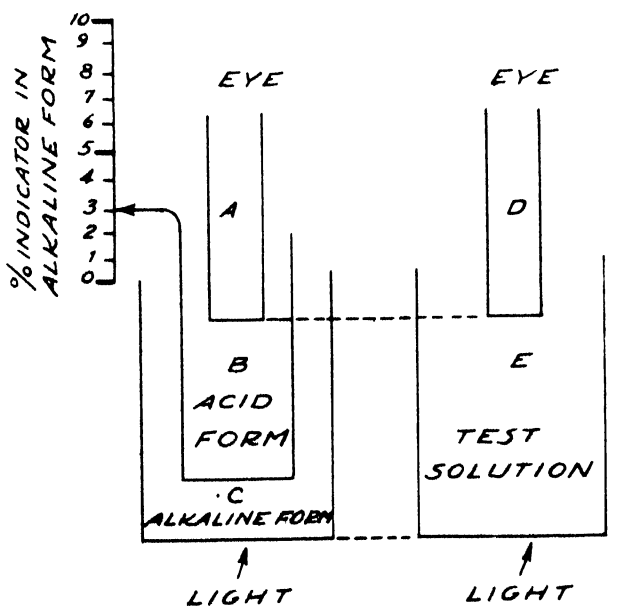


Fig. XII-3. Diagrammatic section of a Bicolorimeter

The first step, as before, is to determine the correct indicator which exhibits an intermediate color when added to the unknown solution. Then a portion of the indicator solution is adjusted to contain a 1:1 ratio of alkaline of acid color. Increasing amounts of this indicator are added to the unknown sample and the resulting colors compared against standard buffers as before, If, for example, the apparent pH values decrease as the amount of added indicator increases, then it is obvious that the acidity of the indicator itself is altering the apparent pH of the solution. Then the ratio of the alkaline to acid form should be increased, the tests repeated until the apparent pH of the unknown does not change when varying amounts of the indicator solution are added.

Highly Colored or Turbid Solutions. Usually electrometric methods must be resorted to. However, if the solutions are highly buffered, they may be diluted with distilled water until the color or turbidity has been suitably diminished. Then the pH is determined as has been described for buffered materials. Another method involves adding talcum to the standards to give the same degree of turbidity, or the Walpole technique can be used since the color of the solution itself and the indicator are additive. The latter is usually more convenient if the color is not too intense.

Sources of Errors. The errors which may be involved in the measurement of slightly buffered solutions have been discussed. It is apparent that the color of a solution containing an indicator will be more intense as the dye concentration is increased. Thus the same concentration of indicator must be added to both the comparison standards and the unknown. The effect of temperature varies a great deal with different indicators, but will usually be smaller when an acid indicator is employed than when a basic indicator is used, as, for example, methyl orange. This effect, for example, is zero with bromphenol

16. Fawcett, E. H. and Acree, S. F., J. Bact., 17, 163 (1929); Ind. Eng. Chem., Anal. Ed., 2, 78 (1930).

blue at 70°, but amounts to 0.3 pH with methyl orange.

The salt error is more serious. The ionization of weak acids is slightly, but noticeably, affected by the presence of neutral salts; and the optical properties of indicators are also altered by salts. The result is that solutions of equal pH but different salt concentration do not always give the same color with an indicator. Unfortunately, the magnitude of this error cannot be predicted and is very irregular. The only way is to determine experimentally the error for various salt concentrations and apply a correction in measurements. This has been done in many cases and has resulted in excluding from use those indicators which show a large salt error. The error can be disregarded when the buffer solutions have about the same ionic strength, and this is the safest way to avoid the error.

TABLE 3. SALT ERRORS AND IONIC STRENGTH

Ionic Strength	0.005	0.05	0.10	0.50
Indicator				
Bromphenol Blue	+0.14	+0.10	0.00	-0.10
Methyl Red	0.00	0.00	0.00	0.00
Bromthymol Blue	+0.12	+0.04	0.00	-0.20
Phenol Red	+0.12	+0.04	0.00	-0.20
Phenolphthalein	+0.18	+0.05	0.00	-0.26
Thymol Blue (alk)	+0.16	+0.05	0.00	-0.12

The magnitude of the error is often negligible, but even with good indicators it is sometimes as large as 0.3 pH unit. Table 3, taken from Kolthoff's "Acid-Base Indicators"[17] shows the error for different ionic strengths of a number of indicators in comparison with a buffer solution having an ionic strength of 0.10. Between 0.01 and 0.2 ionic strength the salt error can usually be disregarded, but as the ionic strength decreases or increases, the error may increase.

Much more difficult to avoid is the "protein error." All protein and even other materials in colloidal solution have a great influence on the color of an indicator because of their adsorption of the indicator. Different colloids behave differently, as do different indicators. Not much has been done toward a systematic determination of the magnitude of protein errors. In general, indicators can be used only when their behavior with the particular protein in question has been checked by the hydrogen electrode.

17. Loc. cit., p. 343.

Addition of alcohol or other polar solvents to water decreases its ionization constant as well as affecting the ionization constants of dissolved indicators. Acidic indicators, such as the sulfonephthaleins, will apparently shift their color intervals to higher pH values, basic indicators to the opposite.

A phenomenon noticed with some indicators is dichromatism. Bromphenol blue and bromcresol purple, for instance, appear one color when viewed in thin layers, and a second in deep layers. Other effects, not so commonly encountered with indicators, include the possibility of oxidation or reduction of the dye, adsorption of one form of the indicator upon colloidal particles within the solution, and the fading or settling out of the indicator upon standing.

Potentiometric Determination of pH.

The second method which can be used for the determination of the pH of a solution depends upon the measurement of the potential produced at an indicator electrode when it is dipping into the test solution. The measurements relative to a reference electrode, are generally carried out with some form of a potentiometer so as not to draw any appreciable amount of current from the reference cell, nor produce any polarization effect at the surface of the indicator electrode.

The Potentiometric Principle. The usual method of measuring two potentials without the passage of appreciable current is by means of a potentiometer, a diagram of which is shown in Fig. XII-4. A D is a uniform slide wire, R is a vari-

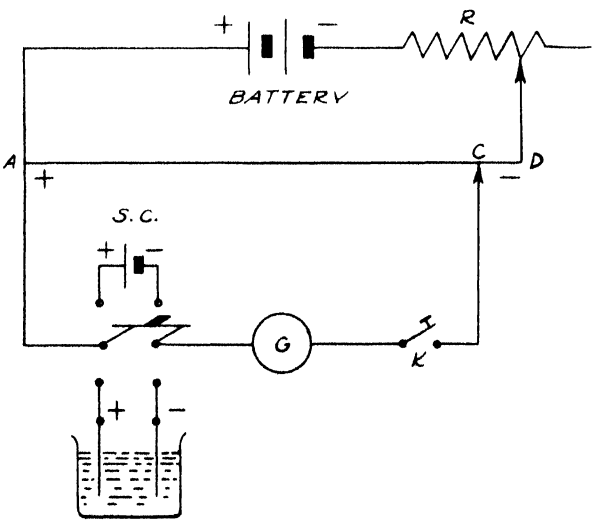


Fig. XII-4. Potentiometer

able resistance, B a battery, SC a standard Weston cell, G a galvanometer, and K a tapping key which completes the circuit only momentarily. The potential drop along the slide wire from A to D is accurately calibrated by setting AC to the potential of a Weston cell and adjusting the resistance R until the galvanometer shows no deflection on closing the key. Thereafter, the two electrodes to be measured are inserted in place of the Weston cell, and the distance AC adjusted until the galvanometer again shows no deflection on closing the key. The potential drop from A to C then is the difference of the potentials of the two electrodes.

A suitable potentiometer for pH measurements shown in Fig. XII-5, is manufactured by the Leeds and Northrup Company. The wiring diagram and

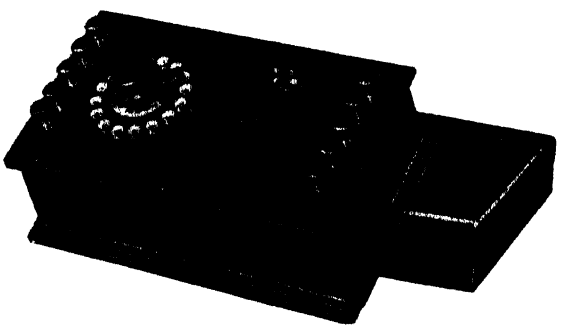


Fig. XII-5. Student potentiometer (Courtesy of Leeds & Northrup)

method of operation of the circuit utilizing this instrument are shown and described in the section on laboratory directions.

In recent years the measurement of potential has been simplified by the introduction of vacuum-tube voltmeters. One of these instruments will draw so little current from the cell under measurement that it may be connected directly to the two electrodes.

Reference Electrodes. A single electrode is not sufficient for pH measurements because there is no accurate method for determining its absolute potential individually. Therefore, it becomes necessary to use a reference electrode whose potential relative to the fundamental, but arbitrarily assigned, hydrogen electrode is known. By international agreement the hydrogen-gas electrode is the standard reference electrode, but it is inconvenient to use and is subject to many restrictions which limit its application.

The most widely used reference electrode, due to its constancy of potential and ease of preparation, is the calomel half-cell, shown in Fig. XII-6. The potential of the calomel electrode depends

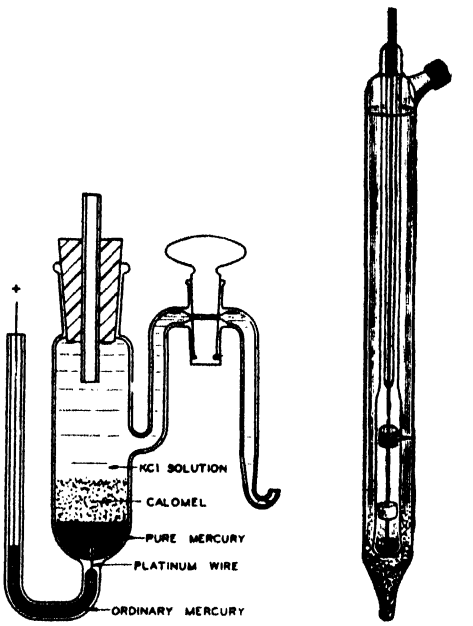


Fig. XII-6. Calomel half-cells. (A) conventional type. (B) modern commercial type. (Leeds & Northrup). Electrical contact made through minute hole in glass

upon the concentration of potassium chloride in the cell. Saturated, normal, and tenth normal potassium chloride solutions saturated with mercurous chloride are used, although the former is easier to prepare. The silver-silver chloride reference electrode is as convenient to use, but is more difficult to prepare. It consists of a silver wire, coated electrolytically with a very thin layer of silver chloride, dipping into a potassium chloride solution of definite composition. The potential of these electrodes against a normal hydrogen electrode at 25° C. is given in Table 4.

TABLE 4. REFERENCE CELL POTENTIALS VS. THE NORMAL HYDROGEN ELECTRODE

Concentration KCl	Calomel	Silver-Silver Chloride
0.10 N	0.3335 v.	0.2880 v.
1.0 N	0.2810 v.	0.2355 v.
Saturated	0.2458 v.	0.2033 v.

For use in solutions in which the presence of chloride ion from diffusion out of the cell might be deleterious, the mercurous sulfate electrode may be used. It is constructed in a manner similar to the calomel electrode but utilizes a sulfuric acid solution rather than a potassium chloride solution.

The reference cell must be connected to the unknown solution by some type of salt bridge. A saturated potassium chloride salt bridge is usually used; but, if the chloride ions are deleterious, a saturated solution of ammonium nitrate or potassium nitrate may be used in its stead. There is a tendency for a potential to be set up at the point of contact of two solutions which is known as the liquid junction potential. By proper design it is possible to limit this or to keep it fairly constant.

Indicator Electrodes. There are a number of indicator electrodes which have been proposed and used as pH measuring electrodes. Of these, only the hydrogen, quinhydrone, antimony, and glass electrodes have been thoroughly established and widely used, and therefore, only these four will be discussed.

The Hydrogen-Gas Electrode. To prepare an electrode which will behave as if it were an electrode of metallic hydrogen, the gas must be absorbed by a good electrical conductor and a material which, itself, has only a very slight solution tension and yet exhibits strong absorptive powers toward the gas. The only metals which exhibit all these properties are the noble metals. Platinum is usually chosen. A piece of platinum foil or wire is coated with a layer of very finely divided platinum, that is, platinum black, deposited electrolytically, in order to increase the surface area. Such a platinized electrode will show a difference of potential toward the solution in which it is placed depending upon the electrolytic solution tension of hydrogen gas and the concentration of hydrogen ions in the solution.

It is not sufficient merely to saturate it with hydrogen, but the platinum black must remain continuously in contact with the gas during the measurement. This is generally accomplished by allowing only the tip of the wire or edge of the foil to dip into the solution, the rest of it being surrounded by gas. The hydrogen gas must be exceedingly pure and a large quantity of this gas is required to secure complete saturation of the solution at the electrode-solution interface.

If the temperature and the pressure of the hydrogen gas are maintained at a constant value, the relationship expressing the e.m.f. of the hydrogen electrode is given by

$$E = 0.0591/1 \log [H^+] = -0.0591\ pH \qquad (24)$$

for a temperature of 25° C.

The advantages of the hydrogen electrode are: (1) It is the fundamental electrode; (2) it exhibits no salt error; and (3) it is useful over the entire pH range.

However, the electrode system is subject to many limitations: (1) It is easily poisoned by various substances such as sulfides, sulfites, calomel, arsenic compounds, etc.; (2) proteins soon cover the electrode and cause it to become sluggish; (3) organic substances able to be hydrogenated interfere; (4) oxidizing and reducing agents cause serious errors; (5) it is inaccurate when dissolved gases are involved in the pH equilibrium; (6) metals more noble than hydrogen or slightly less noble are reduced by the electrode; and (7) it is not adaptable to unbuffered solutions over the range of pH 5.0 to 8.5. The essential use of the electrode is as an auxiliary check upon other types of pH equipment by means of intermittent measurements.

The Quinhydrone Electrode. The quinhydrone electrode is much simpler to construct and use. It consists of a plain platinum wire dipping into the test solution which has been saturated with respect to quinhydrone, an equimolecular compound of hydroquinone and quinone. Quinhydrone is only slightly soluble in water (approximately 4 g. per liter), but it is almost completely dissociated to quinone and hydroquinone. The system constitutes an oxidation-reduction electrode; and the oxidation of hydroquinone to quinone, or the reduction of the latter to hydroquinone, involves the hydrogen-ion:

$$\text{Hydroquinone} = \text{Quinone} + 2H^+ + 2e \qquad (25)$$

The oxidation potential of such a system is given by the expression:

$$E = E^0 + \frac{0.0591}{2} \log \frac{[\text{Quinone}]\,[H^+]^2}{[\text{Hydroquinone}]} \qquad (26)$$

in which $E^0 = 0.6992$ volts.

Since the concentrations of quinone and hydroquinone are equal because of the unique composition of quinhydrone:

$$E = 0.6992 + 0.0591 \log [H^+] \qquad (27)$$

Thus the potential of the quinhydrone electrode changes with the pH of the solution exactly as the hydrogen electrode does.

Obviously anything which will affect the ratio of quinone to hydroquinone will interfere with the use of this electrode. This includes strong oxidizing and reducing agents. Only solutions having a pH less than about 8 or 9 may be measured, since in alkaline medium hydroquinone is readily

oxidized upon contact with air, and since hydroquinone is itself a very weak acid. Colloidal suspensions and certain proteins have apparently specific influences, yet the successful application of the quinhydrone system in many situations indicates that these errors are not very serious.

However, the hydroquinone electrode is quickly prepared, develops its potential rapidly, and can be used in solutions containing dissolved gases, mild oxidizing and reducing agents, salts of metals more noble than hydrogen in the activity series, or unsaturated organic acids. It does exhibit certain salt errors, but these are not particularly serious unless the salt concentration is above 1 molar. Even then, this type of error can be decreased by saturating the solution not only with quinhydrone, but also with either quinone or hydroquinone. One drawback remains, the residual solution is always contaminated for other uses.

A distinct advantage of the electrode is its adaptability to the continuous measurement and control of the pH of many industrial solutions with pH 1 to 9 with a limit of error of 0.1 pH. The use of a solution of quinhydrone in a solvent such as alcohol or acetone permits the attainment of rapid equilibrium in a continuous process.

The Antimony Electrode. Of the various metal and metal oxide electrodes that have been investigated, the most satisfactory is the antimony-antimonous oxide electrode. For the electrode reaction[18]:

$$Sb + H_2O = SbO^+ + 2\ H^+ + 3\ e \qquad (28)$$

the potential of an antimony electrode is given by the expression:

$$E = 0.212 + \frac{0.0591}{3} \log [SbO^+]\ [H^+]^2 \qquad (29)$$

Since the antimonous oxide is very slightly soluble, if the solution is saturated with the oxide,

$$1/2\ Sb_2O_3 + 1/2\ H_2O = SbO^+ + OH^- \quad \text{(ref. 18)} \qquad (30)$$

$$[SbO^+]\ [OH^-] = S_{Sb_2O_3} = \text{ca } 10^{-17} \qquad (31)$$

$$[SbO^+] = \frac{S}{[OH^-]} = \frac{S}{K_W}[H^+] = K'[H^+] \qquad (32)$$

Introducing this expression into equation (29) we find:

$$E = 0.212 + \frac{0.0591}{3} \log K'[H^+]^3 \qquad (33)$$

$$= 0.255 - 0.0591\ pH \quad \text{(ref. 19)} \qquad (34)$$

Equation (33) indicates that the potential of an antimony-antimonous oxide electrode depends upon the temperature, the solubility product of the oxide, the ionization constant of water, the electromotive activity of the metal, and the hydrogen-ion concentration in the solution. If all these factors are held constant except the pH, equation (34) indicates that the electrode changes it potential with the pH in exactly the same way as does the hydrogen-gas electrode.

Generally the potential does not change in an exactly linear manner with the pH of the solution; furthermore, different samples of antimony may not give the same potentials. Therefore, in practice the electrode should be calibrated with two or three standard buffer solutions before use. Also it should be calibrated under the same conditions to which it will be subjected in use; that is, absence or presence of oxygen, quiet or moving solutions. An important secondary equilibrium is set up at an antimony electrode interface when it is submerged in an aqueous solution in contact with oxygen:

$$4\ Sb + 3\ O_2 + 2\ H_2O = 4\ SbO(OH) \qquad (35)$$

Hence the existence of antimonyl (SbO^+) ions at the electrode interface is assured, provided dissolved oxygen has been present. If oxygen is absent, particularly true in the alkaline range, the antimony surface must be oxidized prior to use and the solution saturated with the oxide. Normally, a period of soaking in a buffer solution for several hours prior to use suffices to produce sufficient antimonyl ions at the interface. Under these conditions, a pH measurement may be made over the range of pH 3 to 12 with a limit of error of 0.1 pH unit.

In the practical application of the electrode it was shown that the solubility of the oxide must be negligibly small. Therefore, the presence of strong oxidizing agents or of complexing agents cannot be tolerated. In solutions with a pH lower than 3, the oxide becomes appreciably soluble. Nor can the electrode be used in the presence of metals more noble than antimony.

18. Schuman, R. J., J. Am. Chem. Soc., 46, 52 (1924); Latimer, W. M., "Oxidation Potentials," Prentice-Hall, Inc., New York, 1938, p. 109.

19. Perley, G. A., Ind. Eng. Chem., Anal. Ed., 11, 316, 319 (1939). Hovorka, F. and Chapman, G. H., J. Am. Chem. Soc., 63, 955 (1941).

The antimony electrode does have a distinct advantage for the continuous recording or control of pH in situations where it is applicable, in that the addition of no reagent, solid or gas, is usually required for the measurement. Once prepared, the electrode is usable for extended periods. Being rugged it is useful for continuous plant service, even for measurements involving heavy sludges, viscous fluids, and semi-solids.

Glass Electrode. A thin glass membrane of a certain composition and containing a small amount of water will serve as a conducting medium due to the presence of hydrogen ions which can move in and out of the surface of the glass. If two solutions having a difference in hydrogen-ion concentration are separated by such a glass membrane, any difference in potential between them will tend to establish an equilibrium by electrolytic conduction through the glass. No electrons are involved. As 1 faraday of electricity flows through the glass membrane, using an infinitesimal current, one equivalent of hydrogen ions is reversibly transferred from the more concentrated to the more dilute solution; and, although the mechanism of the process is entirely different from that of the hydrogen gas electrode, the net result is exactly the same. The potential difference between both sides of the membrane is measured with a potentiometer by balancing the potential of a saturated calomel reference, which dips into the test solution, against that of a silver-silver chloride electrode dipping into a buffer solution inside the glass membrane. Owing to the enormous resistance of the glass, about 7 megohms, the small current flowing must be electronically amplified before usual measuring devices can be employed.

The glass electrode consists of a small bulb of low resistance, hydrogen-ion sensitive glass, Corning 015.[20] This thin bulb is sealed to a stem made from a glass exhibiting very much greater resistance to ion transfer (see Fig. XII-7). In this manner ion transfer is confined almost entirely to the special glass membrane, thereby eliminating errors caused by depth of immersion of the electrode in the test solution. The silver-silver chloride electrode and buffer solution are hermetically sealed within the glass bulb at the factory.

All glass electrodes are known to have a small residual e.m.f. across the glass membrane when identical solutions are brought in contact with the inside and outside glass surfaces. The cause of this potential is at present unknown, but seems

20. Corning 015 glass: 72% SiO_2, 22% Na_2O, and 6% CaO.

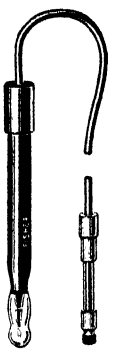


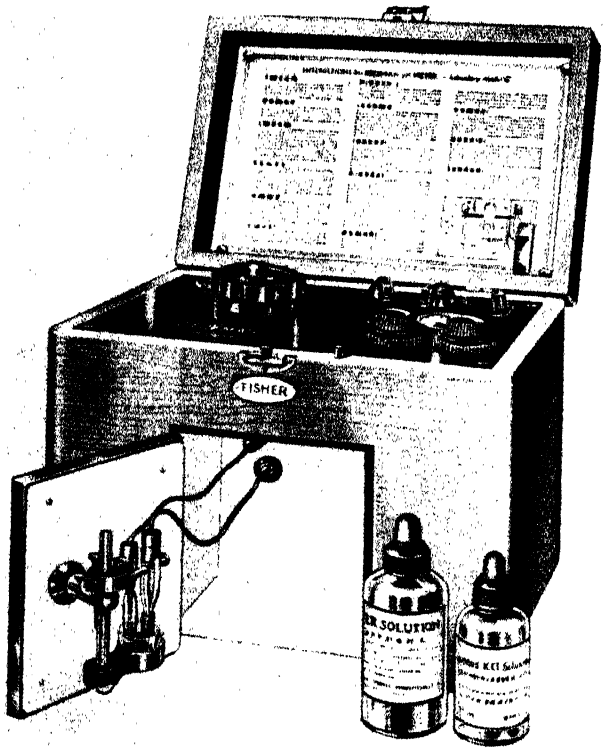
Fig. XII-7. Glass electrode (Courtesy of Fisher Scientific)

to be due to strains in the glass, since this asymmetry potential (A.P.) is usually less with thin than with thick membranes. The asymmetry potential may change slightly from day to day or may be materially altered temporarily by exposure of the glass surface to very strong acid or alkali. It is therefore necessary to calibrate the electrode frequently against some buffer of known pH.

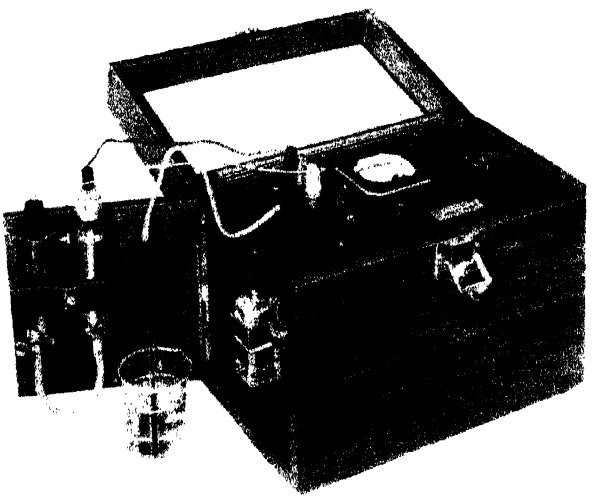
In solutions with a pH greater than 10 the glass electrode gives low values since the membrane transfer may include other ions, so that the e.m.f. no longer measures solely the free energy of transfer of hydrogen ions. This effect is greatest in the presence of sodium ion, since the electrode acts to a certain extent as a sodium electrode. However, the use of special lithium glass electrodes in the strongly alkaline range will decrease the errors appreciably, and extend the useful range of the glass electrode to a pH of 13.5. In a solution of very high acid concentration, below pH 1, the glass electrode again shows a slight error, so that for extremely accurate measurements, its usefulness is limited to the range of pH 1 to 10 unless corrections are applied, or special electrodes substituted.

Glass electrode potentials depend only on the concentration of the hydrogen ions and are absolutely unaffected by the presence of oxidizing or reducing agents, gases, dissolved organic compounds, colloids, highly colored materials, or suspended matter. It can be used in highly unbuffered solutions without introducing an error. Special glass electrodes are also available for use in hot liquids.

A number of portable glass electrode outfits are on the market, both battery and A.C. line operated, as shown in Fig. XII-8.



(Courtesy National Technical Laboratories)
A



(Courtesy Coleman Instruments, Inc.)
B

(Courtesy Central Scientific Co.)
C

Fig. XII-8. Commercial glass electrode outfits. (A) Beckman Model G (Battery Operated). (B) Coleman Model 3D (battery-operated). (C) Cenco (line-operated.)

LABORATORY DIRECTIONS FOR pH

Preparation of Stock Buffer Solutions

1. Potassium Acid Phthalate. The reagent grade commercially available is of sufficient purity. A 0.2 M solution of the salt contains 40.84 g. of the salt dried at 110° C. per liter of distilled water. A crystal of thymol will prevent bacterial action.

2. Potassium Dihydrogen Phosphate. Use 27.22 g. per liter of reagent grade salt which has been dried at 110° C. for a 0.2 M. solution.

3. Potassium Chloride. Use 14.91 g. per liter of the reagent grade material, dried at 110° C., to prepare a 0.2 M solution.

4. Boric Acid. The commercial material should be recrystallized from water and dried between filter papers in a desiccator to constant weight. Use 12.37 g. of the salt per liter for a 0.2 M solution.

5. Hydrochloric Acid. Prepare approximately a 20% hydrochloric acid-water solution by mixing the appropriate amounts of reagents. Analyze gravimetrically as silver chloride according to the usual gravimetric procedures. An appropriate size sample is then weighed out and diluted volumetrically to prepare a 0.2 M solution.

6. Sodium Hydroxide. A saturated solution of sodium hydroxide is prepared in a large silver dish. While protected from air in a desiccator containing ascarite or soda-lime, the sodium carbonate is allowed to settle out. A portion of the clear liquid is pipeted out and analyzed by the usual volumetric procedures. An appropriate size sample is then pipeted out and diluted volumetrically with carbon dioxide-free distilled water to prepare a 0.2 M solution and standardized against potassium acid phthalate. If the molarity is not approximately 0.2 M, a further amount of the saturated sodium hydroxide solution is added to adjust the molarity to 0.2 M, and the solution is again standardized. The prepared solution must be carefully protected from carbon dioxide by means of an ascarite tube, and it must be stored either in a container of alkali-resistant glass or in a bottle whose inside has been coated with ceresine or rubber paint.

Preparation of Indicator Solutions

To prepare solutions of the Clark and Lubs indicators, 0.1 g. of the dye is ground in a clean mortar with the quantities of 0.05 M sodium hydroxide given in Table 5, and diluted with water to 200 ml. for a 0.05% stock solution.

TABLE 5

Indicator	Molecular Weight	ml. 0.05N NaOH
Thymol Blue	456	4.3
Metacresol Purple	382	5.3
Bromphenol Blue	670	3.0
Bromcresol Green	698	2.9
Methyl Red	269	7.4
Chlorphenol Red	423	4.7
Bromcresol Purple	540	5.3
Bromthymol Blue	624	3.2
Phenol Red	354	5.7
Cresol Red	382	5.3
Tetrabromphenol Blue	986	2.0

Solutions of some of the other indicators will require different solvents. Water may be used directly to dissolve methyl orange and alizarin yellow. Phenolphthalein and thymolphthalein should be dissolved in 90% ethyl alcohol.

Determination of pH of a Buffered Unknown by Comparison with Standard Buffers.

1. First determine the approximate pH of the unknown to determine what indicator to use. A universal indicator or test paper may be used, or several drops of bromthymol blue are added to 5 ml. of the test solution. If the resulting color is blue, it indicates that the pH is greater than 7.6. Next add several drops of thymol blue to another test portion: A blue color indicates a pH above 9.6; a yellow color, a pH below 8.0. If the test solution shows a pH above 9.6, continue the testing on fresh portions with alizarine yellow, which is yellow below 10.1 and violet above 12.0.

However, if the resulting color of the bromthymol blue in the original test portion is yellow, the testing is continued on successive fresh test portions with chlorphenol red, bromcresol green, and metacresol purple in the order listed. The color changes of the indicators are given in Table 2, page 139.

If an intermediate virage is ever obtained with one of the indicators during the testing, of course, the pH lies within the indicator's range.

2. Having determined the approximate pH of the unknown, select the correct indicator to use from Table 2. The best indicator will be one for which the pH of the test solution lies at about the middle of the indicator's range.

3. Prepare a series of six buffer solutions according to the directions of Table 1, having pH values separated by 0.2 pH units and overlapping the approximate pH of the unknown. Measure out 5 ml. of the proper stock solution and the proper amount of acid or alkali accurately with a buret or pipet into a graduated cylinder. Then the solution is diluted to 20 ml. with water. The important thing is the correct ratio of the acid and basic component; slight changes in volume will have little effect.

4. Measure into uniform pyrex test tubes 10 ml. amounts of the six buffer solutions. To another similar size test tube add 10 ml. of the test solution. Add the same amount of the selected indicator solution, usually 0.1 to 0.2 ml. from a pipet graduated to 0.01 ml. Mix each solution well by swirling.

5. Observe the test tubes against a white background in daylight but not in direct sunlight. Compare the test solution with the standard buffer solutions. Estimate the pH to 0.1 pH unit.

In no case should a match with the first or last standard in any series of buffers, or the ex-

treme range of an indicator, be taken as an accurate determination.

Operation of Student Potentiometer.

Making Connections. Connect exactly as shown in Fig. XII-9 when using 1.6 volt range. When using 16 millivolt range, the lead shown connected to the post marked 1 should be transferred to 0.01. Give strict attention to the polarity markings. Be sure to include 10,000 ohm protecting resistance P.

Checking Against Standard Cell. First, adjust the working current through the potentiometer. To do this throw switch S to the "Std. Cell" position, and set the dial and slide wire, A and B, to the voltage of the standard cell. The 4-dial rheostat should then be set to give approximately 0.01 ampere through potentiometer, remembering that the voltage of two dry cells in series is approximately 3 volts and that the internal resistance of the potentiometer is approximately 160 ohms. This means that there should be approximately 140 ohms in the 4-dial resistance box. Tap key K-1, note the galvanometer deflection and adjust the rheostat until it is very small, or zero; then tap key K-2 and make final adjustment of the rheostat until galvanometer shows no deflection. The potentiometer is then ready for making measurements.

Measuring e.m.f. Place switch S in position E.M.F., tap key K-1 and note the galvanometer deflection. Reduce or make it zero by adjusting dial switch A and slide wire B. Tap key K-2 and adjust slide wire B until the galvanometer shows no deflection. The sum of the readings of dial switch and slide wire give directly the voltage being measured on the 1.6 volt range. On the 16 millivolt range, the value is read from the dial switch and slide wire, and multiplied by 0.01.

Suppose the dial switch set at 1.1 and the slide wire at 0.0261; the potentiometer reading would be the sum, 1.1261 volts on the 1.6 volt range and 0.011261 volt on the 16 millivolt range.

To make sure that the current through the potentiometer has not changed, return the switch S to "Std. Cell," set the dial switch and slide wire to the voltage of the standard cell and close key K-2. If there is no deflection, the current has not changed; if there is a small deflection, the rheostat must be readjusted to reduce the deflection to zero.

Determination of pH with the Hydrogen Electrode

1. Prepare two hydrogen electrodes. First clean the platinum or gold surface thoroughly with fuming nitric acid or by careful immersion in aqua regia. Dip the electrodes into a 3% solution of chloroplatinic acid containing 1/40% lead acetate. Electrolyze one electrode at a time as cathode using a platinum or palladium anode and a current density of about 1.3 amperes per square decimeter for 5 minutes using two dry cells in series. Gas evolution should be vigorous. A velvety, thin, adherent coating should be obtained. Too thick a coating results in a sluggish electrode. Rinse the electrode with water, and then electrolyze as cathode in dilute sodium hydroxide for a few seconds. Electrolyze as cathode in 10% sulfuric acid for 5 minutes. Wash and keep in distilled water. Do not allow the electrode to become dry or it must be discarded.

2. Place enough standard buffer solution (0.05 M potassium acid phthalate; pH = 4.01 at 25° C. is a convenient standard) to partially cover the electrodes in a round vessel with straight sides. Fit the vessel with a rubber stopper bored with five holes to accomodate the two electrodes, the reference electrode or a salt bridge, a tube for

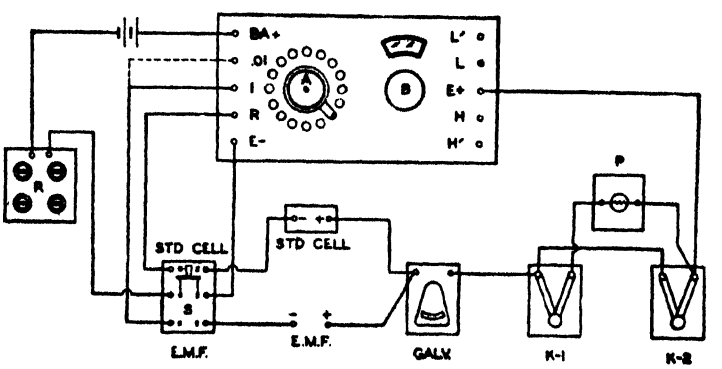


Fig. XII-9. Wiring diagram of student potentiometer (Courtesy of Leeds & Northrop Company)

admitting hydrogen below the electrodes, and a tube for the outlet of the hydrogen.

3. Use either a calomel cell or silver chloride cell as reference electrode. The best practice is to connect the reference cell to the solution by means of a salt bridge rather than placing the cell directly in the solution.

4. Bubble hydrogen from a tank slowly through the solution. Before turning on the main valve of the tank the screw of the diaphragm gauge should be removed entirely.

5. Connect the electrodes to the potentiometer. Use a storage battery or two dry cells as sources of working current. If the student is not familiar with the operation of a potentiometer, he should consult page 151.

6. Measure the difference of potential between the two hydrogen electrodes. It should not be greater than a few tenths of a millivolt. If greater, the electrodes should be cleaned and replated.

7. Measure the difference of potential between a hydrogen electrode and the reference electrode. Calculate the theoretical potential of the hydrogen electrode in the buffer solution. Subtract the calculated value for the hydrogen electrode from the difference in potential as measured. The result is the potential of the reference electrode. Thus all errors such as those due to liquid junction potential, temperature, etc., are thrown into the value of the reference cell and the buffer solution becomes the primary standard.

8. Replace the standard buffer solution with the unknown solution. Bubble hydrogen through the solution for several minutes and then measure the potential difference between the hydrogen electrode and the reference cell. Using the value for the potential of the reference cell determined in step 7, calculate the pH of the unknown.

9. Experience has indicated that the final equilibrium potential of a hydrogen electrode may be attained rather slowly unless the platinized surface is first saturated with hydrogen gas. This is quickly done by electrolyzing a dilute sulfuric acid solution using the electrode as cathode immediately prior to a pH determination. Rinse thoroughly with distilled water before insertion into the test solution.

Determination of pH with the Quinhydrone Electrode

1. Place about 20 ml. of standard buffer solution (0.05 M potassium phthalate, pH = 4.01 at 25° C. is a convenient standard) in a 50 ml. or smaller beaker. Add about 0.05 to 0.1 g. of quinhydrone, and shake or stir for 1 to 2 minutes. Some undissolved quinhydrone should remain.

2. Immerse a clean, bright, platinum or gold wire in the solution and a reference electrode (either a calomel cell or silver-silver chloride cell). The wire is best cleaned with cleaning solution and then rinsed with distilled water.

3. Measure the potential difference of the two electrodes by an ordinary potentiometer.

4. Calculate the apparent potential of the reference electrode from the known pH of the buffer and the measured potential difference. The potential, E, of a quinhydrone electrode is: $E = 0.6992 - 0.0591$ pH (at 25° C.).

5. Replace the standard buffer with the unknown buffer and repeat steps 1-3, above. Using the value for the potential of the reference electrode found in step 4, and the measured difference in potential, calculate the pH of the unknown solution. This method of calculation makes the standard buffer solution the primary standard and eliminates corrections for temperature if both measurements are made at the same temperature.

Determination of pH with an Antimony Electrode

1. Prepare three buffer solutions of known pH between 4 and 10.

2. Place 20 to 25 ml. of buffer solution in a 50 ml. beaker and immerse in the solution a stick of antimony which has been cleaned with sandpaper and rinsed with water. Immerse a reference electrode in the solution.

3. Measure the potential difference between the reference electrode and the antimony stick with a potentiometer in the usual manner.

4. Replace the buffer solution with the second buffer and then the third, repeating the measurement of the potential difference each time.

5. Plot measured potential difference versus pH on a sheet of graph paper. A straight line or nearly straight line should result. Often the electrode readings may show a continual drift; if so, the electrode should be allowed to soak overnight in a buffer before use.

6. Measure the potential difference when the unknown solution is substituted for the buffers.

7. From the graph constructed in step 5 and the potential measured in step 6, read the pH of the unknown.

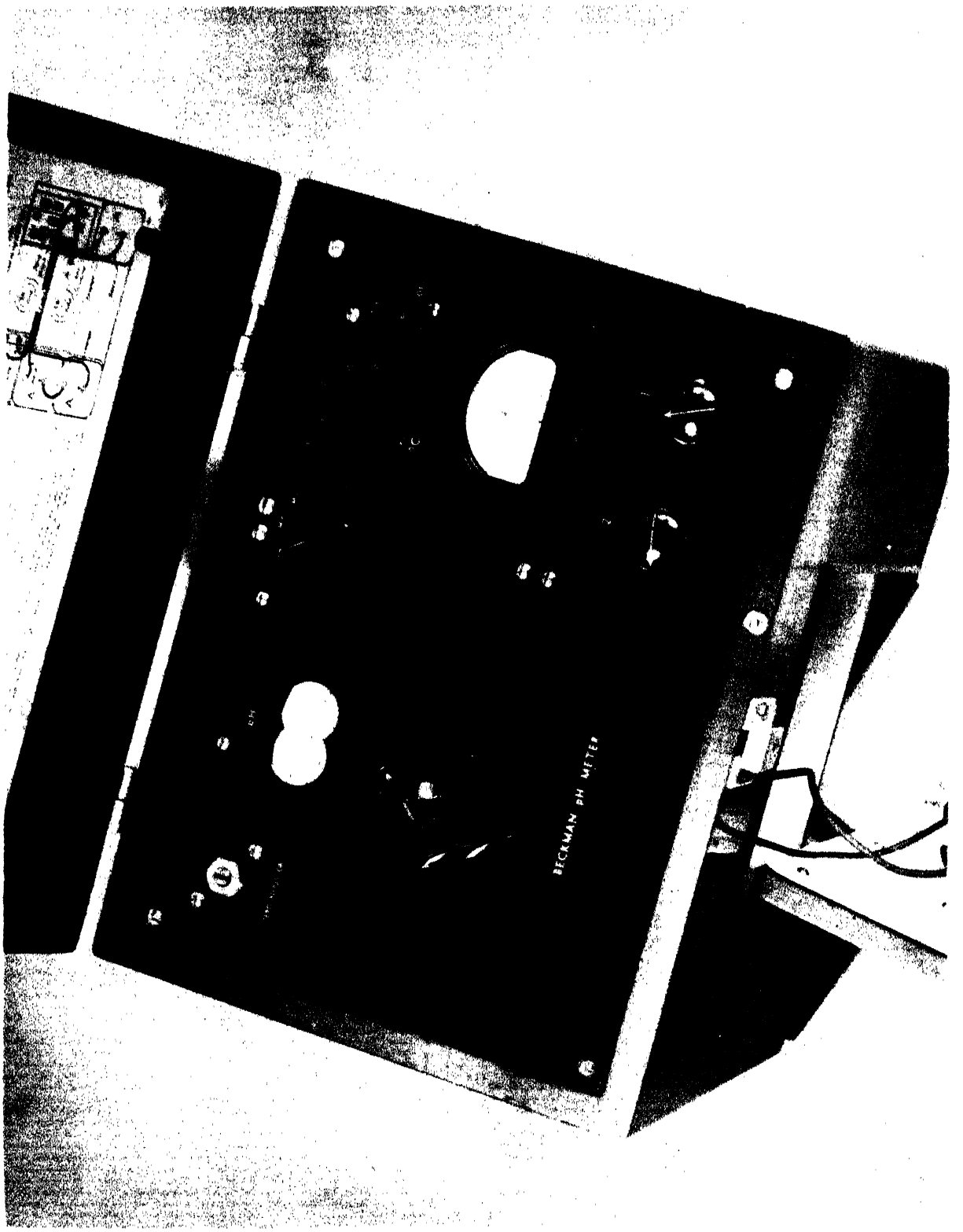


Fig. XII-10. The panel of the Beckman Model G

Determination of pH with Beckman Glass Electrode

General Instructions. (adapted by permission from directions furnished by the National Technical Laboratories). Consult Fig. XII-10.

1. Set the range switch to pH.
2. Move the operating lever in the upper right-hand corner to the vertical or No. 1 position.
3. After a few seconds, adjust the milliammeter needle to zero by rotating control No. 1.
4. Set the temperature compensator to the temperature of the test solution.
5. Check against the standard cell by holding the operating lever in position No. 2 and adjust the milliammeter to zero by means of control No. 2. Return the switch to the vertical position. Adjustment of control No. 2 must be performed each time the temperature compensator is changed; otherwise only infrequent checking is required.
6. Place some standard buffer solution in the small beaker. Close the door. Adjust the instrument as described in 1-5 above.
7. Set the pH dial to the pH of the buffer, lock down the push button in the center of the dial and adjust the milliammeter reading to zero by turning the zero adjustor screw in the upper left-hand corner. It is good practice to standardize against a buffer solution daily and, for precise determinations, it is advisable to make checks before and after each series of tests. Release the push-button.
8. Rinse the electrodes with distilled water and wipe carefully with absorbent tissue.
9. Clean the beaker and half fill it with the test sample. Replace the beaker, raise it into position and close the door.
10. Hold the push button down and rotate the pH dial until the milliammeter reads zero. If the needle fails to remain at zero, readjust control No. 1 (release push button first) and repeat the operation. The pH at the temperature of measurement is read on the dial.
11. "Drifting" of the pH reading will occur if the glass electrode bulb is insufficiently cleaned between samples. When measuring poorly buffered solutions, rinse the electrodes with some of the sample before taking readings.
12. For titrations the push button may be locked down but should be released before the electrodes are removed from the solution or before controls No. 1 and No. 2 are adjusted.

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4. Kolthoff, I. M., "Acid-Base Indicators," 4th Edition, translated by C. Rosenblum, The Macmillan Co., New York, 1937.
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CHAPTER XIII

POTENTIOMETRIC TITRATION METHODS

In the foregoing chapter, we were dealing with the determination of a particular ion activity, or concentration, by measuring the electromotive force between two electrodes: One a reference electrode of constant potential and the other an indicator electrode whose potential was a function of the ion activity in the solution. The differences between the foregoing potentiometric measurements and potentiometric titrations are that, in the latter case, as a rule, absolute potentials, or even potentials with reference to a well-known standard half-cell, are not necessary and the measurements are made while the titration is in progress. Since the plot of e.m.f. readings against the volume of titrating solution will show an abrupt change in potential at the equivalence point of the reaction, any method which will indicate this change is applicable. One electrode serves as an indicator of changes in ion concentration during the titration; and the other electrode is usually one that maintains a constant, but not necessarily known or reproducible, potential. It is important to select as indicator electrode one that will quickly come to equilibrium. Provision must be made for adequate stirring of the solution during the titration. Near the end point the titrating agent is added in small increments and the equivalence point noted as the point of maximum change in e.m.f. per equal increment of titrating agent.

Fig. XIII-1 shows the classical arrangement for potentiometric titrations. The essential components are the titration vessel, two electrodes, a stirrer, a buret, and a potentiometer. For a reference electrode any of the calomel half-cells or silver-silver chloride half-cells, or some of the simpler devices to be described later, may be used.

The outstanding advantages of the potentiometric method are: (1) Applicability to colored solutions or when the end point is evanescent; (2) applicability in many reactions for which suitable colorimetric indicators are not available; (3) applicability in nonaqueous solvents; and (4) precision and sensitivity. However, if a visual indicator method is available, it would generally be preferred, especially for ordinary macro-titrations, because the titration would be much simpler to perform and often more rapid.

Classical Methods. Even though only the increase of potential at the end point is all that is desired in potentiometric titrations, it is of interest to consider what the potential of an indicator electrode would be at the theoretical end point in the classical titration method, and which indicator electrodes will be applicable for each class of titrations.

Neutralization Reactions. In this class of reactions the pH at the equivalence point is dependent upon the kind of material which is formed during the neutralization. The theory of

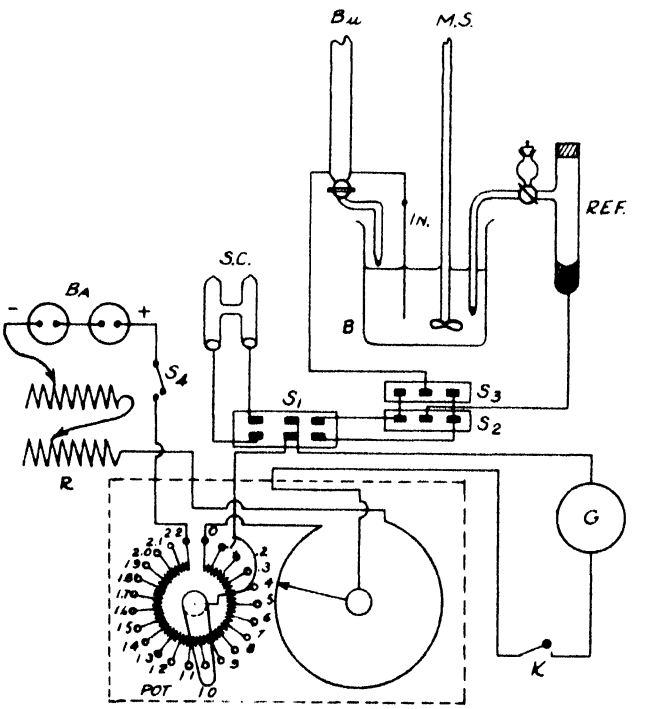

Fig. XIII-1. Potentiometric Titration Circuit and Apparatus. BA, battery; R, resistance; S_1, reversing switch; S_2, S_3, single-pole double-throw switches; S_4, battery switch; S.C., standard cell; IN, indicator electrode; REF., reference electrode, M.S., motor stirrer, G, galvanometer; K, tapping key; Bu, buret, and B, beaker containing solution to be titrated

neutralization is discussed in Willard and Furman's "Elementary Quantitative Analysis," 3rd Edition., pp. 116-129. These authors give formulations which enable the pH to be calculated at

the equivalence point for all of the different types of neutralization reactions. In general, the appearance of a definable inflection is governed by the magnitude of the product of the ionization constant (K_{ion}) and the particular acid or base concentration (c). For practical analytical purposes this product (c K_{ion}) should be greater than 10^{-10}.

Any one of the four hydrogen-ion indicator electrodes previously discussed on pages 146-148 may be used, although the glass electrode is the most desirable. Any other electrode which will respond to changes in pH, even though the electrode may not yield reproducible potentials, may also be used. Certain bimetallic combinations fall in this category, presumably due to a film of oxide forming upon the surface of one metal so that it becomes a metal-metal oxide electrode resembling the antimony electrode.[1]

Regardless of the indicator electrode employed, the potential at the equivalence point is given by the expression

$$E = E^{o} - 0.0591\ pH \qquad (25^{o}\ C.)$$

The pH is calculated from the suitable formulation given in Willard and Furman. The classical potentiometric method is capable of about three times greater sensitivity than titration to the color tint of a reference solution.

Oxidation-Reduction Reactions. The determining factor in oxidation-reduction reactions is the ratio of the concentrations of oxidized and reduced forms of some particular ionic species. In this case the indicator electrode is never a function of the concentration of some particular ion, but only of the ratio of the two states of oxidation of the ion. A bright platinum wire or foil electrode serves to indicate this ratio as given by the expression:

$$E = E^{o} + \frac{0.0591}{n} \log \frac{[Ox]}{[Red]} \qquad (25^{o}\ C.)$$

for the general reaction:

$$Red \rightarrow Ox + n\ e$$

in which E^{o} is the standard electrode potential of the oxidation-reduction system. Without developing the expression,[2] it can be simply stated that the potential at the equivalence point of a generalized reaction,

$$a\ Ox_1 + b\ Red_2 \rightarrow a\ Red_1 + b\ Ox_2$$

is given by the weighted mean of the two standard potentials, E^{o}_{ox} and E^{o}_{red}, representing the standard electrode potentials of the oxidant and reductant respectively:

$$E_{equiv.} = \frac{a\ E^{o}_{ox} + b\ E^{o}_{red}}{a + b}$$

Precipitation Reactions. The ion concentration at the equivalence point of precipitation reactions is determined by the equilibrium constant of the slightly soluble material formed during the titration. The following expression gives the potential of the indicator electrode as a function of the ion concentration $[M^{+n}]$, present during the titration and in equilibrium with a slightly soluble precipitate:

$$E = E^{o} + \frac{0.0591}{n} \log [M^{+n}]$$

where E^{o} is the standard electrode potential for the system:

$$M^{o} \rightarrow M^{+n} + n\ e$$

For a generalized precipitation reaction

$$x\ M^{+n} + y\ B^{-b} \rightarrow M_xB_y$$

for which the solubility product, $K_{s.p.}$, is given by,

$$[M^{+n}]^{x}[B^{-b}]^{y} = K_{s.p.}$$

and the electrode potential at the equivalence point is given by the following expression:

$$E = E^{o} + \frac{0.0591}{n} \log \sqrt[x+y]{K_{s.p.}\left(\frac{x}{y}\right)^{y}}$$

The problem of finding suitable indicator electrodes in precipitation or complex formation reactions causes complications. Theoretically any unattackable metal or nonmetal electrode might serve as an indicator electrode for the concentration of its own ions. Practically, only a few

1. Furman, N. H. and Low, G. W., J. Am. Chem. Soc., 55, 1310 (1933). Also Dietrich, H. G. and Bender, P. J., Ind. Eng. Chem., Anal. Ed., 13, 105 (1941).

2. For a derivation, see Kolthoff, I. M. and Furman, N. H., "Potentiometric Titrations," 2nd Edition, John Wiley & Sons, New York, 1931, pp. 45-47.

have been used successfully, notably silver, mercury, and iodine electrodes.

Sometimes a platinum wire may be used as an indicator electrode if the reaction involves one of the ions in an oxidation-reduction system. For example, in the titration of certain metallic ions with ferrocyanide ion to give an insoluble ferrocyanide salt, if a little ferricyanide ion is added, the ferri-ferrocyanide oxidation-reduction ratio is established (assuming no insoluble ferricyanide salt is formed.) The ferri-ferrocyanide ratio is only slightly affected by the addition of ferrocyanide ions as long as excess metal ions are present, but after the equivalence point has been passed, this ratio will change abruptly due to the addition of excess ferrocyanide ions. The potential of a platinum indicator electrode, therefore, changes abruptly immediately after the end point. Another example is the titration of silver with iodide, using a trace of free iodine to set up an iodine-iodide redox system.

Concentration Cells. The use of suitable concentration cells makes possible a means for the estimation of very small amounts of substances. The primary consideration is that the substance to be determined shall be capable of affecting an electrode in a reversible manner. Furman and Low[3] used two silver-silver chloride electrodes, one dipping into a solution containing an unknown amount (x) of chloride ion and the other into a solution containing the same unknown amount (x) plus a definite known amount (a) of chloride which is added. By having the two solutions identical except for the chloride ion concentrations, the liquid junction potential was eliminated; therefore, the measured e.m.f. is given by

$$E = 0.0591 \log \frac{x + a}{x}$$

This method has also been used to determine fluorides[4] in various solutions, and it is accurate, easy to perform, and rapid.

Detection of the End point. The potential difference between a suitable indicator electrode and a reference electrode is measured after each addition of reagent during the titration until a sudden, large change occurs, marking the end point. Obviously, such a titration is less convenient and longer than one in which a visual indicator is used. The data obtained are usually plotted using the potential as ordinate and the volume of the titrating solution as abscissa. Fig. XIII-2 shows the general shape of the titration curve obtained for neutralization, oxidation-reduction, or precipitation titrations (see Willard and Furman, "Elementary Quantitative Analysis," 3rd Edition, pp. 118, 124, 166, 211.) The end point occurs at the steepest part of the curve, where the rate of change is greatest. In some cases the curve is practically vertical, one drop of solution causing a change of 100 to 200 millivolts in the potential between the two electrodes. In other cases, the slope is more gradual and sometimes the end point is not very readily located. An alternative method of determining the end point from the data is to plot the change in potential per unit volume against the volume. This gives a differential type of curve, Fig. XIII-3, in which the end point is indicated by a peak. However, in precipitation reactions in which the precipitate is formed by the union of ions of unequal valences, the maximum of the differential curve does not exactly correspond with the true equivalence point. It is not usually necessary to plot the curve because the data from which the curve is plotted are sufficient to locate the point of maximum rate of change. The following typical data will illustrate this.

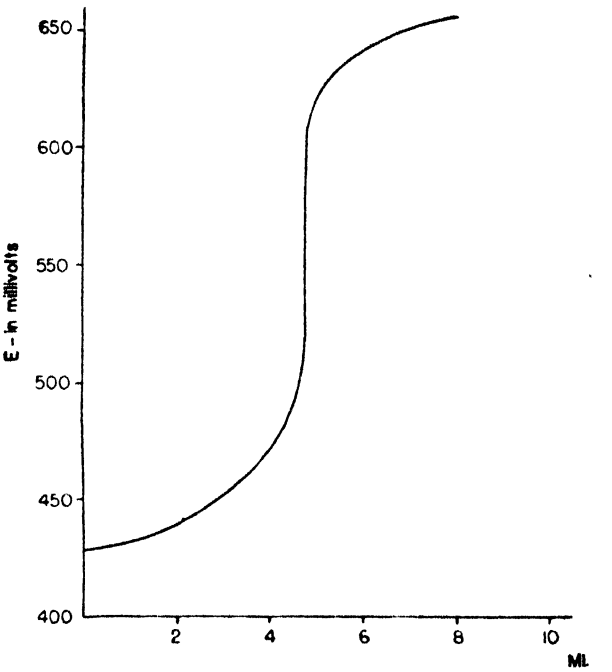

Fig. XIII-2. Titration Curve

3. Furman, N. H. and Low, G. W., J. Am. Chem. Soc., 57, 1585 (1935).

4. Low, G. W. and Pryde, E. H., ibid., 61, 2237 (1939).

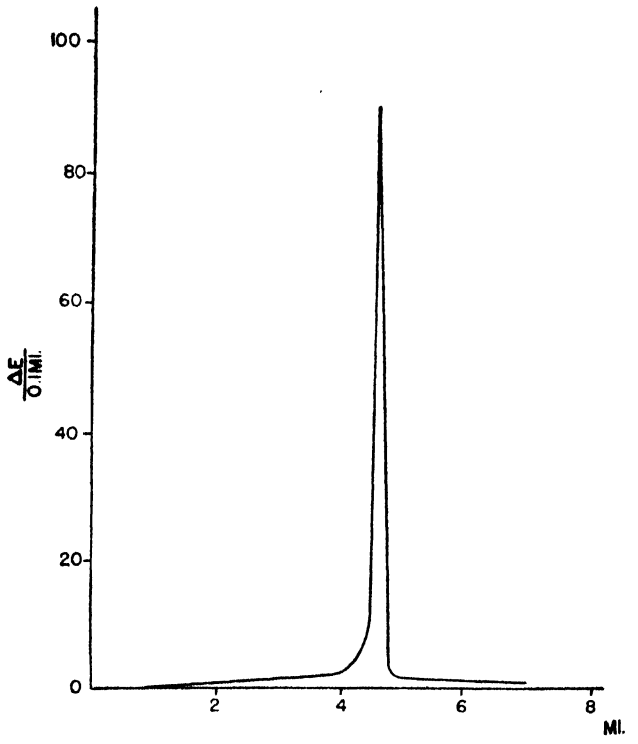

Fig. XIII-3. Differential Plot of Data of a Potentiometric Titration

Total Added ml.	E mv.	Δ E 0.1 ml.
0.0	430	
1.0	435	0.5
2.0	445	1.0
3.0	458	1.3
4.0	473	1.5
4.5	485	2.4
4.6	500	15
4.7	590	90
4.9	620	15
6.0	640	1.8
7.0	650	1.0
8.0	655	0.5

The maximum change per 0.1 ml. of titrating solution occurred after the addition of 4.6 ml. of solution, and 4.70 ml. is therefore, the end point of the titration.

It is usually not necessary to take frequent readings until the vicinity of the end point has been reached.

Simplified Titration Methods. Thus far only the earlier classical method has been considered. One undesirable feature of the earlier work was the use of standard reference electrodes, such as the calomel or similar metal-salt electrodes. Recent work has been directed toward simplifying the electrodes as much as possible and substituting a continuous reading instrument in place of the potentiometer. The inconvenience of the classical electrode pair has been largely eliminated by the use of bimetallic electrode systems and polarized mono-metallic electrode systems, especially for oxidation-reduction work. In the next few sections, these more important simplified procedures will be mentioned.

Titration to the Equivalence Potential. Pinkoff [5] originated this method; Treadwell [6] has modified it somewhat. A reference electrode cell is constructed which duplicates the contents of the solution at the end point of the titration, and thus an electrode dipping into the solution duplicates the potential which an identical indicator electrode will attain at the end point in the solution being titrated. The external circuit consists of a galvanometer, resistance, and tapping key as shown in Fig. XIII-4. During the titration, the deflection of the galvanometer decreases, is zero at the end point, and reverses after the end point has been passed. The titration may be performed rapidly, but the method suffers from several disadvantages: Every titration requires its own prepared, or "bottled," end point solution; two identical electrodes are needed; the system does not attain equilibrium

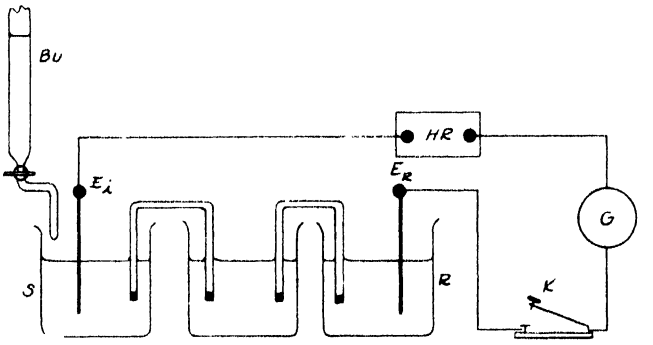

Fig. XIII-4. The Pinkoff System. G, galvanometer; K, tapping key; HR., high resistance; BU, buret; E_i, indicator electrode dipping into S, beaker containing the sample; E_r, reference electrode dipping into the reference solution, R

5. Pinkoff, J., Dissertation, Amsterdam (1919).
6. Treadwell, W. D. and Weiss, L., Helv. Chim. Acta, 2, 680 (1919).

quickly near the end point; and there is no warning of the approach of the end point.

Bimetallic Systems. Bimetallic electrodes have been extensively investigated by Willard and Fenwick[7] and later by Van Name and Fenwick.[8] In many oxidation-reduction reactions, and in some neutralization reactions, a pair of inert electrodes which will respond at different rates to the change in the ratio of oxidant and reductant, may be used to indicate the end point of a titration.

With bimetallic unattackable electrodes the initial voltage at the beginning of the titration varies considerably according to the pretreatment of the electrodes and the condition of the solution as to concentration, acidity, and foreign salts. Upon addition of the oxidizing agent, the voltage falls rapidly to practically zero and remains at this value until the titration is within 0.2 to 0.3 ml. of the end point. A slight rise then gives warning of the approaching end point which occurs with greater sharpness than with the usual electrode combination. The total rise throughout the entire course of the titration is so negligible, as compared to the abrupt change at the end point, that the latter is unmistakable. This break usually amounts to 100-200 millivolts.

The potential difference between two inert electrodes near the end point of an oxidation-reduction titration is primarily a time effect due to a difference in the rate at which the dissimilar electrodes approach equilibrium with a solution of changing composition. This effect is magnified by the enormous increase in sensitivity of the equilibrium potential to a given change in concentration near the equivalence point. The actual magnitude of the end point break is usually less than when a classical reference electrode and indicator electrode are used; however, the break is more abrupt so that no loss in accuracy results.

A less satisfactory, but very interesting, system is the combination platinum with a 10% rhodium-platinum alloy, both unattackable electrodes. Only a slight time lag occurs between the establishment of equilibrium conditions by the two electrodes, as shown in Fig. XIII-5. The alloy electrode attains its single electrode potential more slowly than the platinum electrode. Therefore, if the potential difference between the two electrodes is measured, it will be small until just before the end point, when it will increase rapidly, and then decrease beyond the

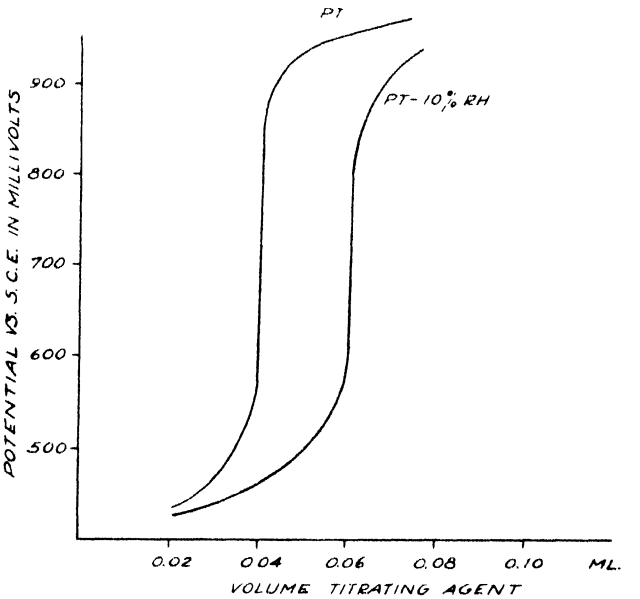

Fig. XIII-5. Single Electrode Potential Curves of Platinum and Platinum-10% Rhodium Alloy at the Equivalence Point

end point. The curve obtained by plotting the potential difference against the volume of reagent will be the well-known differential curve.

The most satisfactory bimetallic combination for oxidation-reduction work is the platinum-tungsten system. The platinum electrode immediately responds to the change in ratio of the oxidant to reductant; whereas the tungsten electrode, which is slightly attacked, exhibits only a very slight dependence upon the ratio as shown in Fig. XIII-6 and thereby, serves as a reference electrode. Fig. XIII-6 also includes a graph showing the potential difference between the two electrodes as a function of the volume of titrating agent. The graph resembles the classical potentiometric curve.

The glass-metal system[9] involves the use of the glass electrode as a reference electrode, and either a platinum indicator electrode for oxidation-reduction titrations or a satisfactory indicator electrode, such as silver in argentometry, for precipitation reactions. The glass electrode serves as a satisfactory reference electrode in any potentiometric titration in which the hydrogen-ion activity remains practically constant throughout the titration. Therefore, for most titrations, the glass electrode will function in solutions that contain excess base, excess acid, or a sufficient amount of an effective buffer. The

7. Willard, H. H. and Fenwick, F., J. Am. Chem. Soc., 44, 2504 (1922).

8. Van Name, R. G. and Fenwick, F., ibid., 47, 9 (1925).

9. Lykken, L. and Tuemmler, F. D., Ind. Eng. Chem., Anal. Ed., 14, 67 (1942).

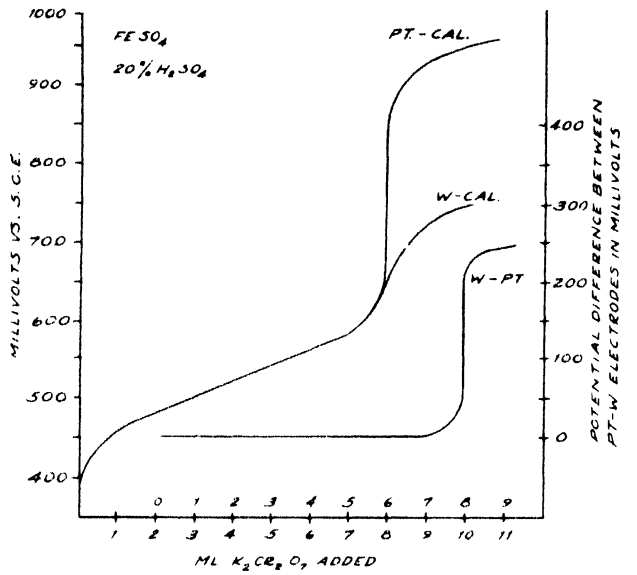

Fig. XIII-6. Single Electrode Potential Curves of Platinum and Tungsten; and the Potential Difference between the Bimetallic System. Pt, platinum; W, tungsten; and Cal., calomel reference electrode.

glass electrode has important advantages over conventional or other simplified reference electrodes: (1) It is readily available for use with very little preparation; (2) it is chemically inert and therefore will not contaminate the solution, and it excludes any effusion from salt bridges; (3) it quickly establishes a definite reproducible potential that does not vary appreciably over short periods of time, even when used with concentrated or nonaqueous solutions. The chief disadvantage in the use of glass-metal systems is that a special meter, which functions accurately on very high input resistances, is required to measure the potential of the electrode system. However, this difficulty is no longer serious since most laboratories are now equipped with pH meters, or suitable electronic voltmeters.

For certain acid-base titrations the combinations of tungsten with either natural graphite, copper, nickel, silicon, cobalt, or silver have been found satisfactory.[10, 11] However, the applicability of any bimetallic pair must be tested with each type of acid or base used, and for each concentration range. This method is now seldom used for neutralization reactions.

Polarized Systems. Willard and Fenwick[12] found that if two identical platinum electrodes, cut from the same wire, are immersed in a solution and a small polarizing current of a few microamperes is applied to the electrodes, they behave as two dissimilar metals and their single electrode potentials respond in a different manner. The exact explanation of their behavior is not entirely known. However, a sudden polarization phenomenon occurs at the end point, and if the potential difference between the two electrodes is plotted against the volume of titrating agent, a differential type curve is obtained. The potential difference developed at the equivalence point is 100-200 millivolts. The simplicity of the electrodes and the sharpness of the end point are distinct advantages, but the suddenness of the end point might result in overstepping it. The end point phenomenon is more distinct the more closely the electrode reactions conform to the requirements of complete reversibility on one side of the end point, and complete irreversibility on the other.

Foulk and Bawden[13] slightly modified the preceding system to make it continuous reading. Two platinum electrodes, connected in series with a high resistance and a galvanometer, are polarized with a potential of 10-15 millivolts, just sufficient to balance the back e.m.f. When a solution of thiosulfate or arsenite is titrated with iodine by means of this simple apparatus, no current flows through the galvanometer until the end point is reached, which is indicated by a permanent displacement of the galvanometer index. The displacement is increased by further additions of iodine. On the other hand, when the reverse titration is made, that is, when iodine is titrated with a solution of thiosulfate or arsenite, the nature of the end point is reversed. Until almost to the end point, the galvanometer will be deflected off the scale. Then, as successive drops of titrant are added immediately preceding the end point, the galvanometer index approaches the zero point of the scale until, coincident with the disappearance of the last trace of iodine, it comes to rest at zero and remains there even after an excess of titrant has been added. For this reason, the method has sometimes been labeled the "dead-stop" end point.

The phenomenon occurring at the end point

10. Furman, N. H. and Low, G. W., J. Am. Chem. Soc., 55, 1310 (1933). Dietrich, H. G. and Bender, P. J., Ind. Eng. Chem., Anal. Ed., 13, 105 (1941).

11. Holt, M. L. and Kahlenberg, L., Trans. Am. Electrochem. Soc., 57, 361 (1930).

12. Willard, H. H. and Fenwick, F., J. Am. Chem. Soc., 44, 2516 (1922).

13. Foulk, C. W. and Bawden, A. T., J. Am. Chem. Soc., 48, 2044 (1926).

is a form of concentration polarization. In the first example only one electrode, the cathode, is polarized. The titrating agent, iodine, must then depolarize this electrode. The anode remains depolarized throughout the entire titration due to the reducing agents present. In the latter example, both electrodes remain depolarized until the end point. At that point, the excess reductant, thiosulfate or arsenite, polarizes the cathode. The method is very sensitive, equilibrium is reached almost instantly, warning of the end point approach is given, and, if overrun, the fact is apparent. These advantages and the simplicity of the circuit, Fig. XIII-7, render the method very useful even though it has seldom been applied to other than iodimetric titrations.

The Differential Titration Method. This method depends upon the concentration-polarization of one of two similar electrodes by some mechanical device which prevents mixing of a small portion of liquid, surrounding one electrode, with the

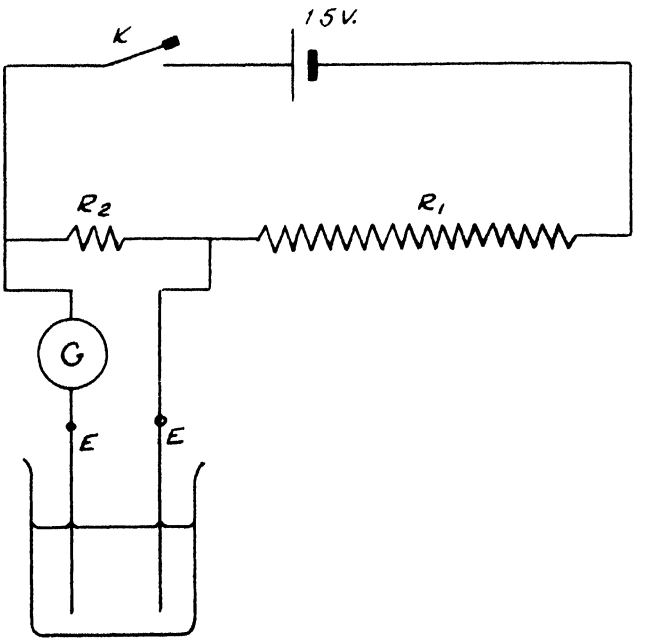

Fig. XIII-7. Foulk and Bawden Apparatus

remainder of the solution. An extremely simple system[14] is shown in Fig. XIII-8, in which a small portion of the solution is withdrawn into a medicine dropper. The potential difference between the two electrodes is measured before and after the addition of each increment of reagent, then the liquid in the dropper is expelled, new solution is admitted to the dropper, and the process repeated. The graph of e.m.f. readings against volume of reagent resembles the usual differential curve. In other systems[15, 16] shown in Figs. XIII-9A and XIII-9B one electrode is sheltered inside a capillary tube or in the delivery tip of the buret. In the latter two instances, the reference electrode potential remains constant, but not reproducible, and the customary S-shaped titration curve will be obtained.

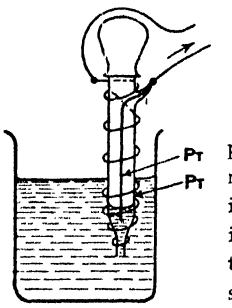

Fig. XIII-8. Differential Apparatus constructed from a medicine dropper and two platinum wires. After each reading near the end point the sheltered portion is forced into the solution by squeezing the bulb.

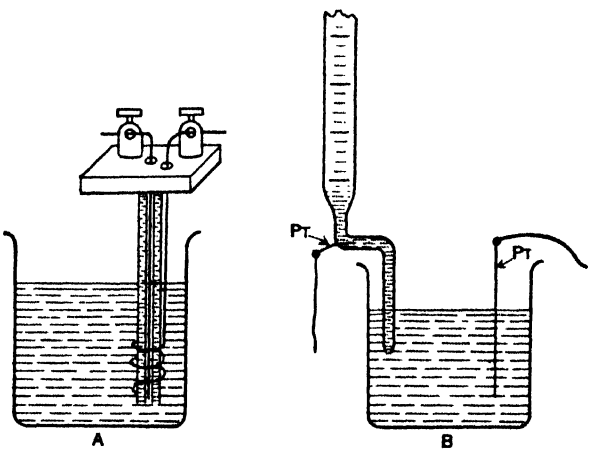

Fig. XIII-9 A: Müller's Capillary Reference Electrode. 9 B: Buret Electrode of Willard and Boldyreff

MacInnes and Dole[17] have developed the differential method until the highest precision is attainable. Their apparatus is shown in Fig. XIII-10. The titration is carried rapidly to an apparent end point without stirring the solution

14. Hall, N. F., Jensen, M. A. and Bächström, S. E., J. Am. Chem. Soc., 50, 2217 (1928).

15. Müller, E., Z. physik. Chem., 135, 102 (1928).

16. Willard, H. H. and Boldyreff, A. W., J. Am. Chem. Soc., 51, 471 (1929).

17. MacInnes, D. A. and Dole, M., ibid., 51, 1119 (1929).

in the reservoir around the reference electrode. Upon stirring with the gas lift pump, L, the titration is finished in the normal differential fashion.

Continuous Reading Methods. In recent years the trend has also been to eliminate the potentiometer or intermittent reading device of the conventional design, if possible, and to substitute a continuous reading instrument. Titrations can then be carried out more rapidly. Several systems have already been mentioned which are based on the use of a high resistance and a sensitive current measuring device. The best continuous reading device for many purposes is some form of a circuit in which an electron tube is used to construct a vacuum-tube voltmeter. If the titration cell is bridged between the cathode and the grid in such a way that the negative electrode of the titration cell is attached to the grid, the voltage difference between the two electrodes may be read on a suitable indicating meter in the output circuit of the vacuum tube. Fig. XIII-11 shows this principle as used in one of the earlier circuits devised by Treadwell.[18]

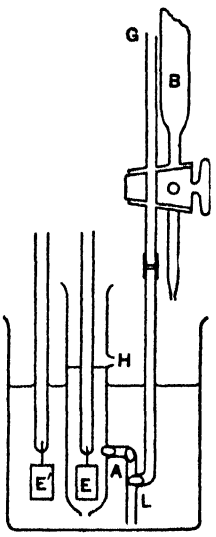

Fig. XIII-10. MacInnes and Dole's Differential Apparatus.

The circuits that are finding most favor for continuous observation during titrations involve a Wheatstone bridge network in the output circuit to compensate for small battery fluctuations or other transient circuit variations. Garman and Droz[19] describe a simple battery operated circuit using tubes with low battery-drain characteristics. The Willard-Hager titrimeter,[20] the Electron Beam Sectrometer of the G. F. Smith Company,[21] and the Fisher titrimeter are A.C. line operated instruments, thus eliminating battery replacement. The latter two instruments dispense with the fragile current measuring device and substitute in its stead a visual cathode-ray, or "magic eye," tube. The sensitivity of the Fisher titrimeter, illustrated in Fig. XIII-12, is such that a potential difference in the electrode system of only 20 millivolts causes a full opening or closing of the "eye." Lingane[22] has described an automatic titration apparatus which both records the curve and regulates the addition of titrating agent.

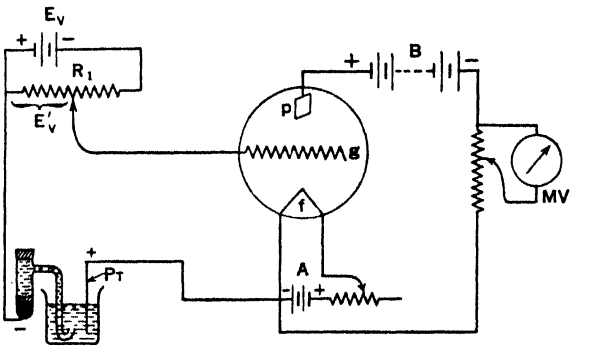

Fig. XIII-11. Early Electronic Vacuum Tube Voltmeter (after Treadwell)

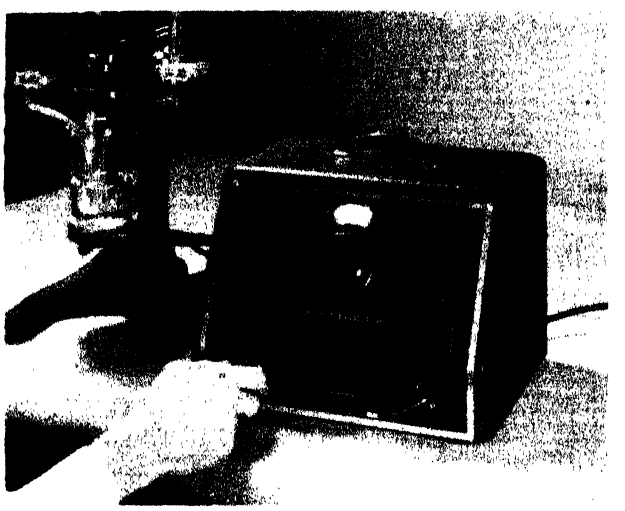

Fig. XIII-12. The Fisher Titrimeter (Courtesy of Fisher Scientific Company)

18. Treadwell, W. D., Helv. Chim. Acta, 8, 89 (1925).

19. Garman, R. L. and Droz, M. E., Ind. Eng. Chem., Anal. Ed., 7, 341 (1935).

20. Willard, H. H. and Hager, O. B., ibid., 8, 144 (1936).

21. Smith, G. F. and Sullivan, V. R., "The Electron Beam Sectometer," G. Frederick Smith Chemical Co., Columbus, Ohio, 1936.

LABORATORY DIRECTIONS

Operation of the Fisher Titrimeter

General Instructions (adapted from the instruction booklet furnished by the Fisher Scientific Co.)

1. Connect the titrimeter stand to the unit by plugging the two large cables with the four- and six-prong plugs into the corresponding sockets mounted on the back of the

unit. Connect the two-prong plugs from the stand and unit into 110 volt, 60 cycle mains. A ground connection from the binding post on the rear of the unit to the nearest water pipe will improve the stability of the titrimeter.

2. Installation of Electrodes. Usually the reference electrode is connected to the left (as the operator faces the stand) porcelain stand-off connector and the indicator electrode is connected to the right stand-off connector.

a. Platinum-tungsten electrode stirrer: The platinum portion of the electrode may be cleaned by immersing the end of the electrode in warm sulfuric-dichromic acid cleaning solution for a few minutes with subsequent rinsing in distilled water. Clean the tungsten terminal projecting from the bottom end of the stirrer by means of a file or fine sandpaper until the bright metal shows. Also see the footnote, page *166*.

To install the stirrer electrode push the sleeve end up through the two 3/8-inch holes which are directly above the beaker support on the titration stand. Slip the pulley over the upper end of the stirrer, continue pushing the stirrer through until its collar fits rather close to the underpart of the lower stirrer support. Tighten the headless setscrew in the pulley.

To complete the electrical circuit, insert a brush in each of the 1/8-inch holes (they face the operator at the level of the stirrer sleeves), then the springs, and finally the machine screws which act as retainers. Do not tighten the screws beyond what is necessary to produce definite contact between collar and brush. Connect a short copper wire from the lower machine screw to the right porcelain stand-off connector. The upper connection is made through the electrode support and to the stand.

b. Glass electrode: The glass electrode in all cases is mounted on the right-hand side of the stand (as the operator faces the "eye"), the main lead being connected by a knurled screw to a porcelain stand-off connector; the other lead, from the shield, being plugged into a small socket just below the porcelain connector, to ground it.

c. Stationary or nonstirring electrodes: These electrodes, platinum, tungsten, silver, and silver-silver chloride, are mounted without springs and brushes in the lower stirrer support in front of the stand by thrusting their plastic caps through the holes and tightening the knurled screws. When used in conjunction with the calomel electrode, these electrodes are connected to the left porcelain stand-off connector.

The platinum and tungsten electrodes may be cleaned according to the procedure outlined under section 2-a. The silver electrode may be cleaned by rubbing with fine emery paper until the silver has a bright lustre.

3. The instrument is turned on by turning the Eye Control knob clockwise. While the instrument is warming up, the glass stirrer is inserted into the two metal parts in front of the stand unless the platinum-tungsten stirrer electrode is used. The end of the stirrer is extended into the pulley wheel and locked there by tightening a setscrew in the collar of the pulley. The pulley belt is then placed around the pulley wheel and the end of the motor shaft.

4. Calibration. After the instrument has warmed up for 2 or 3 minutes, it should be calibrated each time before use.

a. Volts scale:
   (1) Set Cal-Use control to CAL.
   (2) Set dial to the desired value.
   (3) Adjust Eye Control to null (until eye is at a just open position or until a fine line is observed.)

If the instrument is calibrated at 0.0 on the dial, readings will be directly in volts. If the calibration point is 0.5, then the dial range will be from -0.5 to +0.5 volts; and if calibration is done at dial reading of 1.0, the scale will then cover the range -1.0 to 0.0 volts. Each of the Voltage Scale divisions represents 0.01 volt.

b. pH scale:
   (1) Immerse the glass and calomel electrodes in a buffer solution of known pH.
   (2) Set Cal-Use control to USE.
   (3) Set dial to read the pH of the buffer on the pH scale.
   (4) Adjust the Eye Control until the Eye just opens.

5. Measurement of Oxidation-Reduction Potentials. Calibrate the instrument according to the directions given in 4-a. Rinse the electrodes well, and immerse the electrodes in the sample to be measured which is placed on the platform below the electrodes. Set the Cal-Use control to USE and adjust the dial until the Eye is in the null position (just open).

Read the volt scale on the dial, and subtract the volts scale reading used for calibration to obtain the value of the oxidation-reduction potential. If it becomes impossible to obtain a null with the available scale readings, it is an indication that some other calibration point should have been used in step 4-a, in order to shift the voltage range to include the range of potentials which it is desired to measure.

6. Measurement of pH. Calibrate the instrument according to the directions given in 4-b. Rinse the electrodes well, and immerse them in the sample to be measured which is placed on the platform below the

electrodes; leave the Cal-Use control in the USE position, and adjust the pH scale on the dial control until a null position is obtained (Eye just open). The scale reading obtained is the pH of the test solution.

7. Plotting a Titrimetric Curve. To plot a titrimetric curve, the titrimeter is set up and calibrated according to the preceding directions. The procedure described under measurement of pH is used for acidimetric or alkalimetric titrations, and the corresponding procedure described under measurement of oxidation-reduction potentials is used for this class of titrations.

a. Place the solution to be titrated on the stand and turn the dial until the eye indicates null. Read the pH or voltage from the corresponding scale.

b. Record or plot this reading opposite zero ml. of titrant.

c. With the stirrer turned on, add a small volume of titrant. Allow a few seconds for the titrant to react and then adjust the dial until the eye indicates null.

d. Record or plot this reading opposite the ml. of titrant added up to this point.

e. Continue this process of adding, readjusting the dial, and recording the volume and dial reading until several milliliters of titrant have been added past the point of noticeable change in the dial reading.

8. Routine Procedure. First the titrimetric curve must be plotted as described in the preceding section. The dial reading at the equivalence point is found by passing a horizontal line from the point of inflection to the dial reading axis. For subsequent titrations simply place the samples on the stand, turn on the stirring motor, set the dial at the predetermined dial setting, and add the titrant until the eye indicates the null position - that is, just opening or closing, depending upon the direction in which the titration is carried out.

For rapid, routine work it is advisable to make a preliminary dial setting at some value which will precede the final end point setting and titrate to this point first in order to avoid overstepping. Subsequently, the exact end point is determined by advancing the dial setting to the final predetermined end point value, and cautiously titrating drop by drop.

Operation of the Cenco Titrimeter

Insert the divider into the input terminals of the instrument. Tighten into position. The high potential side of the source should be connected to the divider terminal nearest the front of the instrument, and the low potential side of the source should be connected to the divider terminal nearest the rear of the instrument. Adjust the electrical zero of the instrument as outlined in sections 1, 2, 3, and 4 under "Voltage Measurements." For making measurements of external voltages, set the selector switch to the "5 V" position and multiply the scale reading by the factor 2.5.

Voltage Measurements.

1. Set the selector switch to the WARM UP position. Set the meter polarity switch to NOR. position. Check mechaninal zero of meter.

2. Insert the line cord into a 110-120 volt, 60 cycle source. Turn the power switch to the ON position.

3. Allow the instrument to warm up for about 30 minutes. It may be used with a shorter warm-up period if the electrical zero is checked frequently.

4. Set the selector switch to the ADJUST ZERO position and then rotate the zero adjust knob until the meter pointer is at zero. If it is impossible to adjust to zero, see note below.

5. Connect the potential to be measured to input terminals on the left-hand side of the instrument.

6. Rotate Selector switch to .5 volt or .1 volt position, whichever is desired, and read meter.

7. When the meter polarity switch is in the NOR. position, the input terminal nearest the front of the instrument is the positive terminal; and, when the meter polarity switch is in the REV. position, the input terminal nearest the front of the instrument is the negative terminal.

Notes

1. Always turn the selector switch to the WARM UP position before turning the power switch to ON or OFF.

2. If at any time it becomes impossible to set the meter pointer to zero by rotating the zero adjust knob when the selector switch is in the adjust zero position and the instrument has been on for at least 30 minutes, proceed as follows:

a. Set zero adjust knob to approximately its mid-position.

b. Remove plug button at lower right-hand side of instrument case.

c. A slotted shaft will be visible inside the chassis through the hole from which the plug button was removed. Insert screw driver in the slot of the shaft and rotate until the meter pointer is at zero.

d. Replace plug button.

LABORATORY DIRECTIONS FOR POTENTIOMETRIC TITRATIONS

Classical Methods

General Instructions for Classical Methods

1. Into a 400 ml. beaker, place the solution to be titrated. Introduce a mechanical stirrer, the indicator electrode, and the reference electrode.
2. Place the titrating solution in a buret with an offset stopcock and clamp the buret in such a manner that the solution can be run into the beaker without splashing.
3. Connect the reference and indicator electrodes to a potentiometer or electronic voltmeter. Be sure there are no bubbles in the reference electrode system. Directions for assembling and operating a potentiometer have been given on page 151 of Chapter XII.
4. Stir the solution at a moderate rate avoiding any splattering of solution out of the beaker. Read the potential difference and record this reading and the buret reading.
5. Add 1-2 ml. of titrating solution, stir for 30 seconds or until the potential becomes constant, and record the readings.
6. Repeat the addition of solution and the readings until the equivalence point has been reached and passed. Additions of as much as 5 ml. may be made at the beginning. Near the equivalence point the additions should be reduced in size to only 1 drop. The equivalence point is the point of greatest rate of change of potential with addition of reagent. There is little warning of the approach of the equivalence point.
7. Plot buret readings as abscissa and potentials as ordinate. Draw a smooth curve through the points. The equivalence point is the volume corresponding to the steepest portion of the curve.
8. Plot on another graph the change in potential divided by the number of milliliters of reagent added as ordinate against buret reading as abscissa. The equivalence point is the volume of titrating agent at which the curve reaches a maximum.

Determination of the Equivalence Point in an Acid-Base Reaction. The instructor will assign an acid and base to be titrated and the electrode system to be used. Prepare 0.1 N solutions and use 25 ml. for the titration unless instructed otherwise. Proceed as directed under general instructions. Suggested titrations are:

ortho-Phosphoric acid with sodium hydroxide.
Boric acid in presence of mannitol[23] with sodium hydroxide; hydroxylamine, hydrazine, or aniline salts with sodium hydroxide.
Sodium carbonate or nitrite (in the cold), or borate with hydrochloric acid.
Di- or tri-ethanolamine with hydrochloric acid.

The quinhydrone electrode is prepared as described on page 152, and the antimony electrode as described on page 152. No standardizations with buffer solutions are required with the antimony electrode since only changes in potential are important. If the glass electrode is to be used, proceed as described on page 154, but use the large external glass and calomel electrodes furnished for titration work. A shielded cable is furnished to attach the electrodes to the pH meter. Adjust the stirrer carefully so that it does not strike the electrodes.

Determination of the Equivalence Point in an Oxidation-Reduction Reaction. The instructor will assign a reaction to each student. Prepare 0.1 N solutions of the titrating agent and the substance to be titrated. Place 25 ml. of the substance to be titrated in the beaker. Use a bright platinum wire or foil for the indicator electrode and either a calomel or silver-silver chloride reference electrode. Proceed as directed under general instructions.
Suggested oxidation-reduction systems are:

Arsenious or antimonyl ions in 10-20% hydrochloric acid with potassium bromate.[24]
Chromate and vanadate ions with ferrous sulfate by the Willard and Young method.[25]
Cobalt in presence of citrate and ammonium hydroxide, with potassium ferricyanide.[26]
Ferrocyanide ions in 1 N hydrochloric acid with potassium bromate.[27]
Manganous ions in presence of pyrophosphate with potassium permanganate.[28]

23. Foote, F. J., Ind. Eng. Chem., Anal. Ed., 4, 39 (1932).
24. Zintl, E. and Wattenberg, H., Ber., 56, 472 (1923).
25. Willard, H. H. and Young, P., Ind. Eng. Chem., Anal. Ed., 6, 48 (1934).
26. Chirnside, R. C., Cluley, H. J. and Proffitt, P. M. C., Analyst, 72, 354 (1947).
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Determination of the Equivalence Point in a Precipitation Reaction.

A. Using a Silver Indicator Electrode for Argentometry.

The instructor will assign some substance to be titrated with silver nitrate or other soluble silver salt. Prepare 0.1 N solutions of each and use 25 ml. of the substance to be titrated. Use a calomel or silver-silver chloride reference electrode, separated from the solution by an ammonium or potassium nitrate salt bridge. Use a polished silver wire as the indicator electrode.

B. The Iodine-Iodide Redox Electrode.

An example of the use of a oxidation-reduction system to indicate the end point of a precipitation reaction, involving the titration of iodide ions with silver ions, will be illustrated by the use of an iodine-iodide electrode, whose potential can be represented by the expression:

$$E = E^{o} + \frac{0.0591}{2} \log \frac{[I_2]}{[I^-]^2} \qquad (25^{o}C.)$$

A bright platinum wire will indicate the ratio of iodine to iodide ion. Since iodine is only slightly soluble in an aqueous solution, an excess of iodine assures a constant concentration of iodine, and therefore, the electrode potential will vary only as a function of the iodide ion concentration. If the metal iodide formed possesses an order of solubility comparable to silver iodide, the hydrogen-ion concentration will exert a profound influence upon the potential, due to the following secondary reaction and the corresponding potential expression postulated by Sammet:[29]

$$3\ I_2 + 3\ H_2O \rightleftharpoons 6\ H^+ + IO_3^- + 5\ I^-$$

$$E = 1.16 + \frac{0.0591}{10} \log \frac{[H^+]^{12}\ [IO_3^-]^2}{[I_2]}$$

Reagents.

Alcoholic iodine solution, 10%

Sulfuric acid, 5 N.

Standard solutions of silver nitrate, 0.1 N, and potassium iodide, 0.1 N.

Procedure. Place 25 ml. of the potassium iodide solution in a 250 ml. beaker, add 1-2 ml. of 10% alcoholic iodine solution, 2 ml. of 5 N sulfuric acid, and dilute to about 50 ml. Proceed to titrate with the silver nitrate solution as directed under general instructions, except to use an ammonium or potassium nitrate salt bridge.

29. Sammet, Z. physik. Chem., 53, 641 (1905).

SIMPLIFIED METHODS

Analysis of the End point Phenomenon with Platinum-Tungsten Bimetallic System

Place 25 ml. of 0.1 N ferrous sulfate into a 250 ml. beaker, add 10 ml. of concentrated sulfuric acid, 5 ml. syrupy phosphoric acid, and dilute to 50 ml. Immerse a platinum wire or foil electrode, a tungsten wire electrode,[30] and a standard reference half-cell into the solution to be titrated. Connect the platinum and tungsten electrodes separately to opposite ends of a single-pole double-throw switch. The center tap of the switch and the standard reference half-cell is connected to the potentiometer or other measuring device.

Proceed with the titration as directed under general instructions. After the addition of each increment of titrating agent, measure the potential of the tungsten electrode against the standard reference half-cell, and the potential of the platinum electrode against the same reference cell. In step 7 of the directions, plot the two electrode potential curves. In place of step 8, plot the differential curve for the potential difference between the tungsten and platinum electrodes at each stage of the titration.

Repeat the titration with a fresh 25 ml. portion of ferrous sulfate, this time using the tungsten wire as a reference electrode and the platinum wire as the indicator electrode. Plot the results as directed in step 7 of the general directions.

Detection of the End point with Glass-Metal Electrode System

The glass electrode serves as a satisfactory reference electrode in any potentiometric titration in which the hydrogen-ion activity remains practically constant throughout the titration. Therefore, in most oxidation-reduction and argentometric titrations, the electrode will function as a useful reference electrode. A pH meter or electronic voltmeter which functions on a high input resistance is required to measure the potential of the electrode system.

Suggested Titration Systems

1. Mixtures of iodide and chloride ions, or of thiocyanate and chloride ions, or any of the

30. The tungsten electrode should either be polished or immersed for 5-10 seconds in a crucible of sodium nitrite which is barely molten and then washed with distilled water. If the fusion mixture is too hot, the tungsten will quickly dissolve.

individual ions, may be titrated with 0.1 N silver nitrate in a titrating medium of 0.05 N nitric acid using a polished silver wire as indicator electrode.

2. Mixtures of permanganate and vanadate ions titrated with 0.1 N ferrous sulfate in a cold titrating medium of 6 N sulfuric acid using a platinum indicator electrode.

3. Ferrous sulfate titrated with ceric sulfate, or dichromate ion titrated with ferrous sulfate, in a titrating medium of 6 N sulfuric acid using a platinum indicator electrode.

Measuring E.M.F.'s with the Beckman pH Meter

Connect the upper jack to the glass electrode, the lower jack to the indicator electrode. Set the range switch to "+MV." When the cell reverses polarity, move switch to "-MV." Balance the meter with controls No. 1 and No. 2 and measure by holding down the push button and rotating the slide wire until the galvanometer needle returns to zero. Then release the button. If the needle fails to remain at zero, readjust control No. 1 and repeat.

The scale reads from 0 to 1300 millivolts, each small division representing 10 millivolts, when the instrument is used as an electronic voltmeter. The zero adjuster and temperature compensator are automatically disconnected from the circuit when the switch is in the "MV" positions.

Procedure. Place 25 ml. of the solution to be titrated into a 400 ml. beaker, add the correct amount of titrating medium to stabilize the pH of the solution, and dilute to 100 ml. Insert the mechanical stirrer and the electrode assembly. Connect the electrodes to the pH meter, and proceed with the titration as directed under general directions.

Bimetallic Electrode System used in Precipitation Reaction.

The titration of zinc solutions with potassium ferrocyanide in the presence of a very small amount of potassium ferricyanide is another example in which an oxidation-reduction ratio is used to detect the end point in a precipitation reaction. If the tungsten-platinum bimetallic system is used, the titration can be further simplified. The tungsten electrode serves as the reference electrode, and the platinum electrode indicates the change in the ratio of ferricyanide ions to the ferrocyanide ions which occurs abruptly after the equivalence point has been reached.

Reagents

Zinc sulfate solution, 0.1 N.
Potassium ferrocyanide solution, 0.1 N.
Potassium ferricyanide solution, 0.001 N.

Procedure. Place 25 ml. of a 0.1 N zinc solution in a 250 ml. beaker, add 1.0 ml. of 0.001 N potassium ferricyanide, and dilute to 50 ml. Insert the bimetallic electrode assembly and a stirrer. Titrate with 0.1 N potassium ferrocyanide as directed in the general instructions. The solution should not be acid.

Detection of the End point with Polarized Mono-Metallic Electrode System

Fig. XIII-7 on page 161 illustrates the arrangement of the apparatus. B is an ordinary 1.5 volt dry cell; E, E are platinum wire or foil electrodes; G is a sensitive galvanometer, 10^{-7} amp/mm.; R_1 is a high resistance, usually 100,000 ohms; and R_2 is a resistance or potentiometer whose value is between 1.0 and 1.5% of R_1, preferably a radio potentiometer which can be adjusted so that the galvanometer is just brought to zero when at least one electrode is polarized: that is, dipping into a solution of sodium thiosulfate or arsenite. A motor stirrer is not shown, but must be used. The essential feature of the procedure is the adjustment of the two resistances so that the potential difference between the two electrodes is only 10 to 15 millivolts, just sufficient to balance the back e.m.f.

Reagents.

Iodine solution, 0.1 N containing potassium iodide also 0.1 N.

Sodium thiosulfate or sodium arsenite solution, 0.1 N.

Procedure. Place 25 ml. of the solution to be titrated into a 250 ml. beaker, introduce the titration assembly, and proceed with the titration. If either sodium arsenite or sodium thiosulfate is being titrated with iodine, adjust the galvanometer index to zero at the beginning of the titration. The galvanometer index will remain at zero during most of the titration; the end point is indicated by the first permanent displacement of the galvanometer index. The displacement is increased with further additions of iodine solution.

If iodine solution is being titrated with either reducing agent, the galvanometer index is adjusted to zero with both electrodes dipping into a solution of either the sodium arsenite or thiosulfate. At the beginning of the titration of the iodine solution, the galvanometer index will be

off the scale, but when nearly all of the iodine has been reduced the index will come into view. As successive drops of the reducing agent are added, the rest point of the galvanometer index oscillations will approach the zero of the scale until, coincident with the disappearance of the last trace of the iodine, it comes to rest at zero, and remains there even when an excess of thiosulfate solution has been added.

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CHAPTER XIV

CONDUCTOMETRIC TITRATION METHODS

Except under abnormal conditions of very high voltages or high-frequency currents, a solution, like a metallic conductor, obeys Ohm's law. Thus, if the applied electromotive force, E, remains constant, the current, I, will vary inversely with the resistance of the solution, R. The conducting power of a solution - the conductance, C - is taken as $\frac{1}{R}$ and is expressed in reciprocal ohms, that is, ohms^{-1}, sometimes called mhos.

$$C = \frac{1}{R} = k\frac{a}{\ell}$$

where C = conductance;
R = resistance;
k = specific conductance;
a = area of conductor;
ℓ = length of conductor.

The specific conductance, k, is in reality the conductance of a cube of material 1 cm. in length and 1 sq. cm. in cross section.

As a solution of an electrolyte is diluted the specific conductance will decrease, since fewer ions to carry the electric current are present in each milliliter of solution. If, however, all of the solution should be placed between two electrodes, 1 cm. apart, and large enough to contain the whole solution, the conductance will increase as the solution is diluted. This is due largely to a decrease in inter-ionic attraction effects for strong electrolytes and to an increase in the extent of ionization for weak electrolytes. If 1 g. equivalent weight of the solute is present, then the conductance of such a solution is known as the equivalent conductance, Λ. The equivalent conductance will be equal to the specific conductance times the volume, V, in cubic centimeters containing 1 g. equivalent weight. Thus, if c is the concentration of a solution in gram equivalents per liter,

$$\Lambda = kv = 1000\frac{k}{c}$$

As the concentration is decreased, the equivalent conductance increases but, for strong electrolytes, seems to approach a limiting value, Λ_∞ known as the equivalent conductance at infinite dilution. The equivalent conductance at infinite dilution of weak electrolytes cannot be determined directly by extrapolation of conductances measured at increasing dilutions because the conductance is increasing quite rapidly at the most dilute solutions measurable. The Λ values of weak electrolytes are usually calculated from the equivalent conductances at infinite dilution of the respective ions.

At infinite dilution the ions are independent of each other and each contributes its part to the total conductance, thus

$$\Lambda = \ell_+ + \ell_-$$

where ℓ_+ and ℓ_- are known as the ion conductances at infinite dilution of the cation and anion, respectively. If 1 g. equivalent weight of solute is present at infinite dilution, there will be the same number of charges present regardless of the nature of the solute. The quantity of electricity that can pass through an electrolyte - that is, the conductance - depends on the product of the number of ions, the charge carried by each ion, and the velocity with which each ion moves. If then, the total charge is constant, the equivalent conductance of a solution at infinite dilution can depend only on the velocities of the ions. The different velocities, or mobilities, of the various ions are responsible for the different equivalent conductances at infinite dilution of the ions as listed in Table 1.

TABLE 1. MOBILITY OF SOME IONS AT 25° AT INFINITE DILUTION

H_3O^+	350	OH^-	193
Li^+	42	Cl^-	76
Na^+	51	Br^-	78
K^+	75	I^-	76
NH_4^+	75	NO_3^-	71
Ag^+	63	HCO_3^-	47
$1/2\ Mg^{++}$	55	CH_3COO^-	41
$1/2\ Ca^{++}$	61	ClO_4^-	74
$1/2\ Ba^{++}$	65	IO_3^-	40
$1/2\ Zn^{++}$	56	$1/2\ CO_3^{--}$	70
$1/2\ Cu^{++}$	57	$1/2\ C_2O_4^{--}$	74
$1/2\ Pb^{++}$	73	$1/2\ SO_4^{--}$	80
$1/2\ Fe^{++}$	54	$1/2\ CrO_4^{--}$	82
$1/3\ Fe^{+++}$	68	$1/3\ PO_4^{---}$	80
		$1/3\ Fe(CN)_6^{---}$	97
		$1/4\ Fe(CN)_6^{----}$	101

The mobility of most ions at infinite dilution increases 2% to 2.5% per °C. rise in temperature due to the increase in the ionic migration

velocities. Consequently, a conductance cell should be allowed to attain thermal equilibrium before proceeding with conductance measurements. More concentrated solutions of strong electrolytes behave in about the same manner but weak electrolytes may show abnormalities. The conductance of weak electrolytes depends largely upon the degree of dissociation which is dependent upon the temperature, but the dependence varies from substance to substance.

Theory of Conductometric Titrations. Unlike potentiometric measurements, conductometric measurements are not specific for any ion, since, as already stated, conductance is a function of the number of ions and their mobility. A change in conductance may occur, therefore, when ions are removed and substituted with other ions by precipitation, by forming a complex, or by forming a slightly dissociated molecule. Thus, Ag^+ and Cl^- form AgCl, Ag^+ and CN^- form $Ag(CN)_2^-$, and H_3O^+ and OH^- form water. This is the principle of conductometric titrations: The substitution of ions of one mobility by ions of another mobility.

The conductance is measured after the addition of each increment of reagent, and the points thus obtained are plotted to give a graph which, as a rule, consists of two straight lines of different slopes intersecting at the equvalence point. The accuracy of the method is greater the more acute the angle of intersection and the more nearly the points of the graph lie upon straight lines. It is necessary that the volume of the solution shall not change. In order to minimize the dilution effect, the titrating agent should be at least tenfold more concentrated than the solution being titrated. The latter should be as dilute as feasible. A satisfactory correction may be obtained for the dilution effect if each conductance is multiplied by the ratio, total volume to initial volume.

A more acute angle is sometimes possible through proper choice of ions. For example, the lithium and acetate ions have a smaller conductance than most other ions. Therefore, the conductometric titration curve, Fig. XIV-1a, obtained for the titration of silver acetate with lithium chloride, would be much sharper than if another silver or chloride salt had been used, such as silver nitrate and potassium chloride, Fig. XIV-1b. Other examples will be discussed in the section on applications.

In contrast to potentiometric titration methods, but similar to the amperometric method to be discussed later, measurements near the equivalence point have no special significance. In fact, due to hydrolysis, solubility, or dissociation of

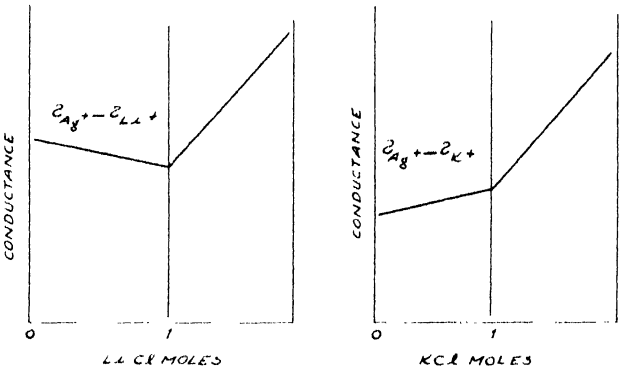

Fig. XIV-1. (a) Titration of 0.02 N silver acetate with 0.1 N lithium chloride. (b) Titration of 0.01 N silver nitrate with 0.1 N potassium chloride

the reaction product, values of conductance measured near the equivalence point are usually worthless in the construction of the graph since one or both curves will give a rounded portion at this point. However, the main points of interest lie either before or after the equivalence point where the excess of one or the other common ion will repress the hydrolysis, solubility, or dissociation of the reaction product. Thus, conductometric titrations can sometimes be used where visual or potentiometric methods fail, such as for reactions where there is considerable hydrolysis or solubility at the equivalence point. Examples include the direct titration of weak acids by weak bases, the displacement titration of salts of moderately weak acids or bases by strong acids or bases, and many precipitation reactions involving moderately soluble substances. The method enjoys the advantage of being as accurate in dilute as in more concentrated solution.

On the other hand, due to the large conductances of any foreign salts which do not take part in the reaction, the conductometric method has a limited application, since the accuracy is mainly determined by the relative change of conductance of the solution during the reaction and upon addition of excess of reagent. Fig. XIV-2 illustrates the role played by each ion present in the solution to the total conductance, assuming no inert salts are present other than those formed during the titration.

Oxidation-reduction titrations usually cannot be

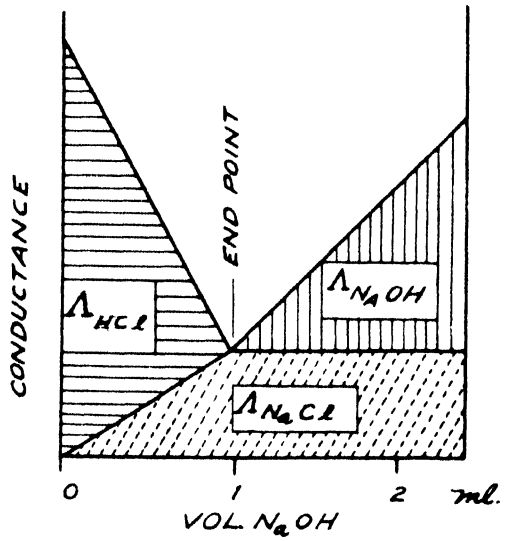

Fig. XIV-2. Illustration of the constitution of a conductometric titration curve. Neutralization of 0.1 N HCl with 1.0 N NaOH

performed conductometrically because the solutions are commonly strongly acid, and thus the original conductance is so high that small changes are not detectable.

Under optimum conditions, the precision to be expected from conductometric titrations is 0.5%. The time consumed in an individual titration is 10 to 15 minutes.

A high-frequency alternating current must be employed to overcome any polarization effects set up at the electrodes due to the counter e.m.f. of ions able to undergo electrode reaction. This requirement poises difficulties for the detection of the balance point in any measuring device.

Performance of Conductometric Titrations

Measurement of Conductance. The classical method of measuring conductance was originated by Kohlrausch, who used a Wheatstone bridge as shown in Fig. XIV-3. The conductivity cell (z) forms one arm of a Wheatstone bridge, a standard fixed resistance (W) forms another arm, and a calibrated slide wire resistance with end coils provides the remaining two arms. High-frequency alternating current (1000 cycles) is supplied to the bridge either by a vacuum-tube oscillator or small induction coil. Capacitances and inductances, as well as resistances, are of importance in obtaining balance in a Wheatstone bridge when alternating current is used. A variable condenser (C) must be connected in parallel with the fixed resistance and, after the resistances are balanced as well as possible, various capacitances are inserted until a sharper setting is obtained, before the final resistance adjustments are made. To detect the point of balance, a telephone (T) is usually used; however, it is necessary to work in a room undisturbed by noises - a distinct disadvantage.

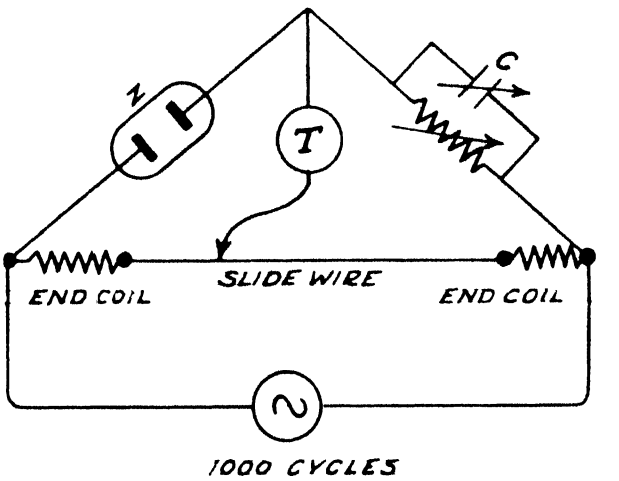

Fig. XIV-3. Kohlrausch's conductivity bridge

Fortunately, the telephone can be replaced by other devices so that the point of balance can be detected in a visual manner. The Leeds and Northrup, or any other make, AC galvanometer provides one of the simplest pieces of apparatus for determining the point of balance of a Wheatstone bridge. A satisfactory circuit is shown in Fig. XIV-4. Ordinary 60 cycle alternating

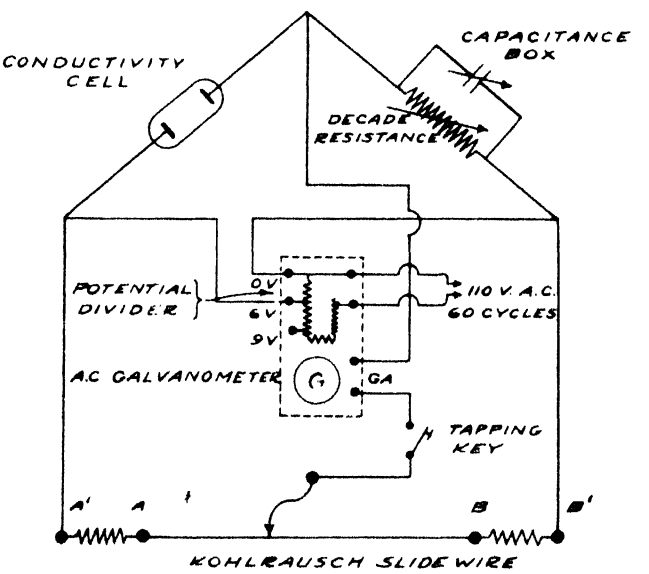

Fig. XIV-4. Conductivity bridge using ordinary 60 cycle current and an alternating-current galvanometer for balance

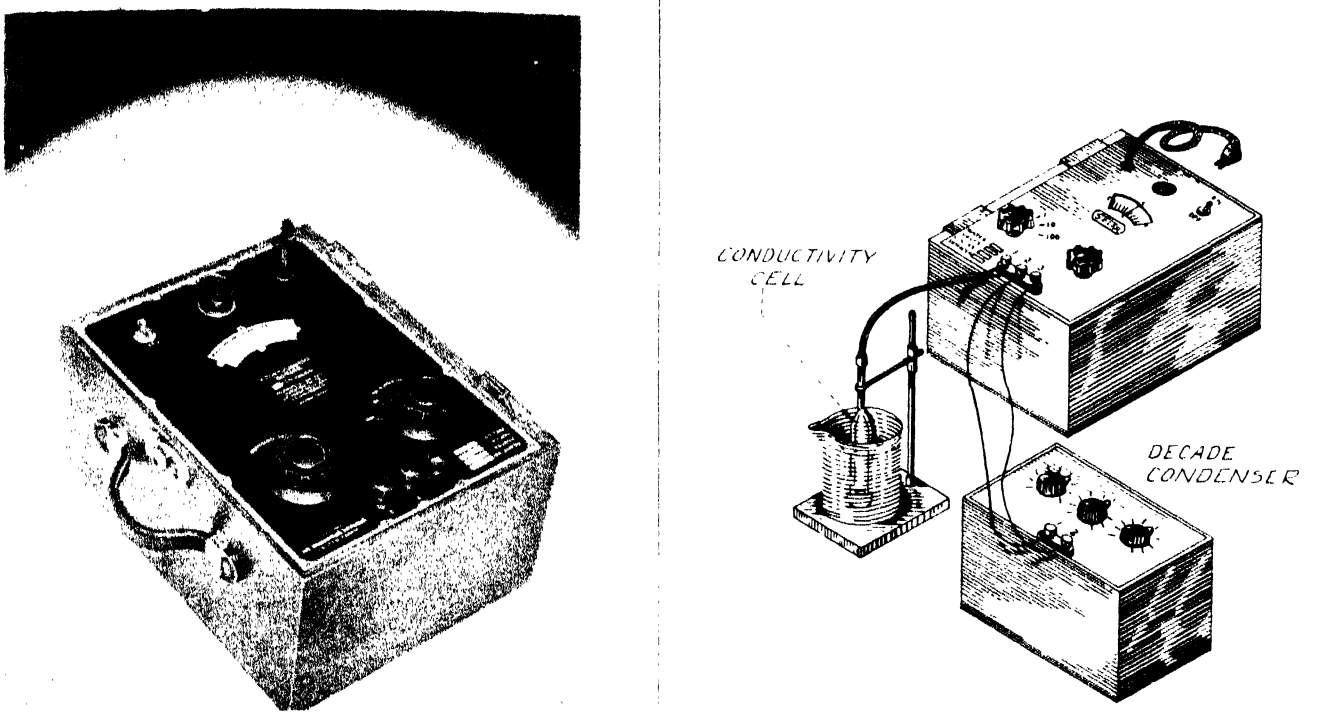

Fig. XIV-5. Conductivity Bridge Model RC - 1B (Courtesy of Industrial Instrument Company)

current from a 110 volt main is suitable, instead of a source of high-frequency current. Although the bridge cannot be balanced as accurately as with higher frequency currents, the precision is suitable for titration work. Some care must be exercised to prevent any heating effects occurring at the electrodes.

A more convenient apparatus than the AC galvanometer is the Conductivity Bridge manufactured by the Industrial Instruments Company. (Fig. XIV-5). Measurements are made by means of an AC bridge with an input voltage of 3 volts and 60 cycle current, which is obtained through a step-down transformer (Fig. XIV-6). The bridge output voltage is connected to a single-stage vacuum-tube amplifier, which in turn is coupled to a cathode-ray tube null indicator. The cathode-ray tube, or "Magic eye," replaces the delicate galvanometer usually associated with bridge measurements and is not affected by variations in line voltage. Any resistances from 0.2 to 250,000 ohms can be measured. An auxiliary capacitance enables a sharper adjustment of the balance point to be attained. Some models have built-in 1000 cycle current sources for the bridge current.

It is also possible to have a direct reading conductance meter. Such an instrument has been described by Garman.[1] It is a vacuum tube circuit with a self-contained bridge, detector, and oscillator operating from either AC or DC mains. The resistance is directly proportional to the readings on the microammeter.

Conductance Cells for Titration Work. Conductometric titration cells must be designed with vertical electrodes and of such a shape that, as solution is added, not much change occurs in the cell constant. If the cell is initially filled to a point which is well over the electrodes, a small change in the height of the liquid will make a relative small dilution error due to a small change in the cell constant. The electrodes must be vertical in order to prevent the formation of a film of precipitate in precipitation reactions. Several titration cells with different cell constants - that is, different size electrodes and at varying distances apart - should be available for work with solutions of quite different conductances. With low-conductance solutions the electrodes should be large and close together. A

1. Garman, R. L., Ind. Eng. Chem., Anal. Ed., 8, 146 (1936).

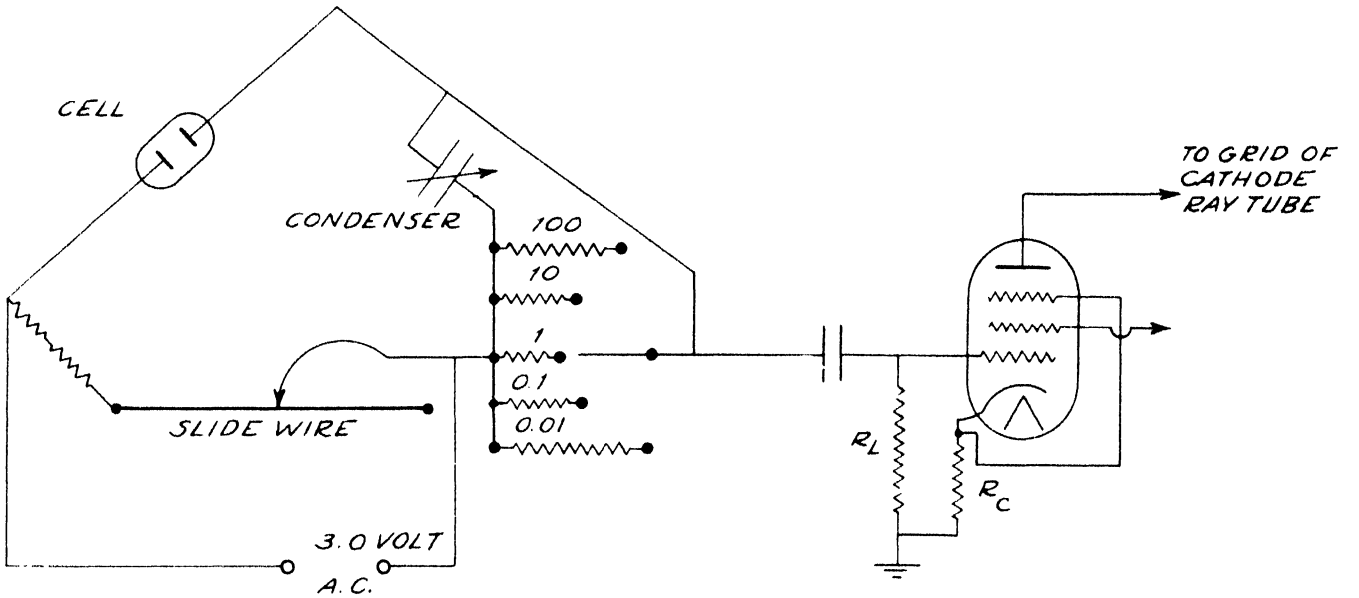

Fig. XIV-6. Circuit diagram of Industrial Instrument Company's Conductivity bridge showing the bridge circuit and amplifier tube

typical cell is shown in Fig. XIV-7. The electrodes are usually 1 sq. cm. in area and constructed from sheet platinum, which is lightly platinized to minimize capicitance effects. An electrode separation of 2 cm. is suitable for most work, although for precipitation work the distance may be greater. A convenient electrode for continuous measurement of intermittent measurements on industrial process solutions is the dipping type electrode shown in Fig. XIV-8.

No provisions need be made for thermostating the cell, except to allow the cell to attain thermal equilibrium with its surroundings, which should be at constant temperature, before commencing the titration. Care should be exercised not to warm the cell with the hand during agitation to mix the reagents.

It is difficult to measure accurately the dimensions and other factors of a conductivity cell, so that it is common practice to calibrate a cell by measuring in it a solution of potassium chloride of known concentration and conductance. From the measured cell resistance and the known conductance, a cell constant, K, is calculated such that

$$C = \frac{K}{R}$$

For titration purposes, one does not need to know the absolute conductance but is interested only in the relative effects as the titration progresses. The reciprocal of the measured cell resistance is therefore plotted against volume of titrating solution and one does not need to calibrate the cells.

Application of Conductometric Titrations.

Neutralization reactions. In the neutralization reactions of strong bases with strong acids, or the reverse, there will be an initial rapid decrease in conductance due to the replacement of hydroxyl ions with a mobility of 193 by the anion of the acid with a mobility of only 40 to 80 (see Table 1). Beyond the equivalence point, the conductance will again increase rapidly due to the large mobility of the hydrogen ion - 350. Fig. XIV-2 shows the conductometric titration curve. The equivalence point does not occur exactly at pH 7, since the mobilities of the hydroxyl and hydrogen ions are not equal; however, the error is very small. Solutions as dilute as 10^{-4} N may be accurately determined, Fig. XIV-9, although the only application would probably be if the solution were deeply colored.

Several factors must be considered when titrating acids or bases of intermediate strength: (1) An increase in conductance occurs due to the increased ionization of the salt formed. (2) A decrease in conductance occurs due to the decrease in ionization of the acid or base through common-ion effect. (3) An increase in conductance occurs as the initial concentration of acid or base decreases due to increased ionization of more dilute solutions. The shape of the

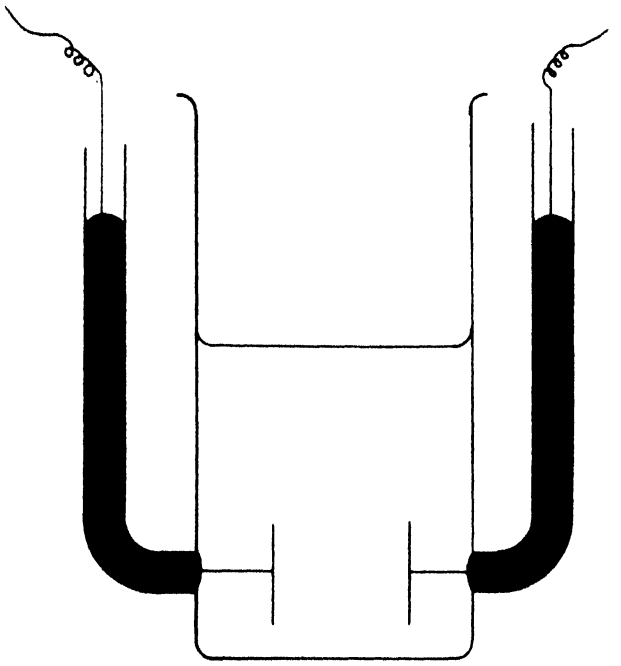

Fig. XIV-7. Typical conductance cell for titrations

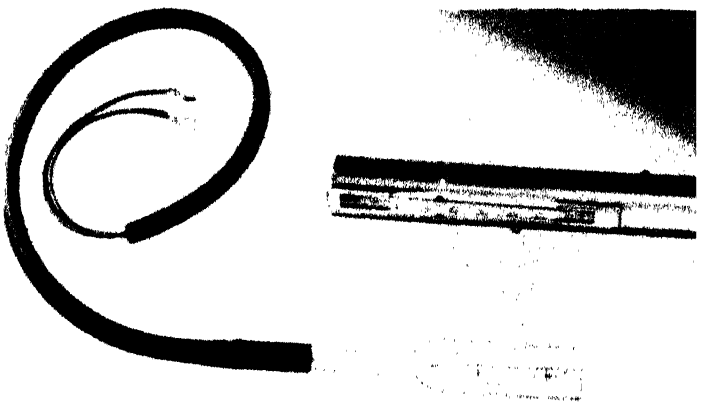

Fig. XIV-8. Dip cell and Metal Protecting Cover. (Courtesy of Industrial Instrument Company)

conductance curve will vary, therefore, with the strength of the acid or base and its concentration as shown in Figs. XIV-10a and XIV-10b. Addition of ethyl alcohol often reduces the ionization sufficiently to yield a region of linear conductance preceding the equivalence point. This addition will usually not be necessary if the ionization constant divided by the concentration of the acid or base to be titrated is less than 5×10^{-3}.

In the titration of very weak acids with a strong base, or the titration of very weak bases with a strong acid, the initial conductance is very small, but will increase during the neutralization as the salt concentration increases. Pronounced hydrolysis renders the values of conductance measured near the equivalence point useless; thus experimental points for the construction of the two graphical lines must be selected that are considerably removed from the end point so that the hydrolysis will be repressed by the action of one or the other common ion. These data will yield straight lines. If the acid or base is extremely weak, the hydrolysis is so extensive that the titration does not yield useful results. However, solutions of very weak acids or bases, in which the product of the ionization constant and concentration exceeds 10^{-11}, may be satisfactorily titrated. Fig. XIV-11 illustrates a typical curve.

If the titration of a weak acid is carried out with a weak base, such as ammonium hydroxide, the equivalence point often can be accurately determined because there is practically no increase in conductance after the equivalence point (see Fig. XIV-12).

Righellato and Davies[2] suggested two excellent procedures to enable the equivalence point to be located with greater precision in the titration of weak acids. In the first method, the titration is carried out with ammonium hydroxide as previously mentioned. If this is not successful, a second titration is carried out on an identical sample with potassium hydroxide. The conductance curves are practically identical preceding the equivalence point since the mobilities of the potassium and ammonium ions are essentially equal. Beyond the equivalence point the conductance curves are straight lines for both reagents, but of quite different slopes. The intersection locates the equivalence point as shown in Fig. XIV-13. The second procedure involves the addition of a small amount of ammonium hydroxide, which partially neutralizes the acid, then completing the titration with sodium hydroxide. When all the acid has been neutralized, the

2. Righellato, E. C. and Davies, C. W., Trans. Far. Soc., 29, 431 (1933).

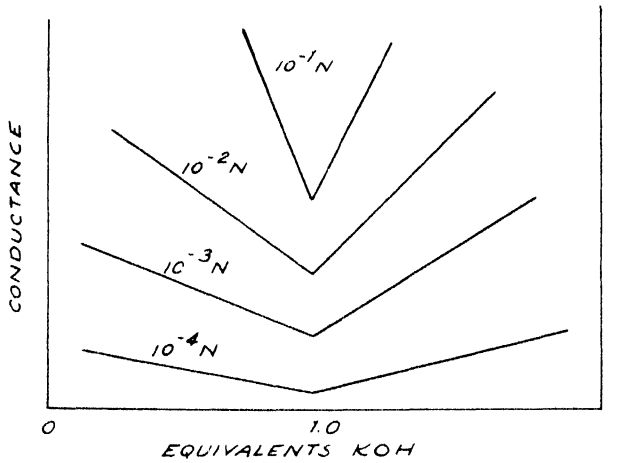

Fig. XIV-9. Effect of dilution upon the conductometric titration curve of a strong acid with a strong base

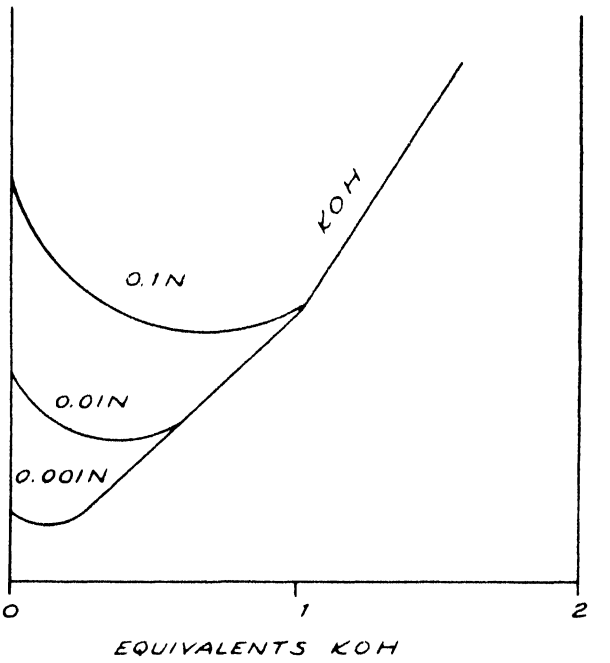

Fig. XIV-10b. Effect of strength of weak acid upon the shape of the conductometric titration curve

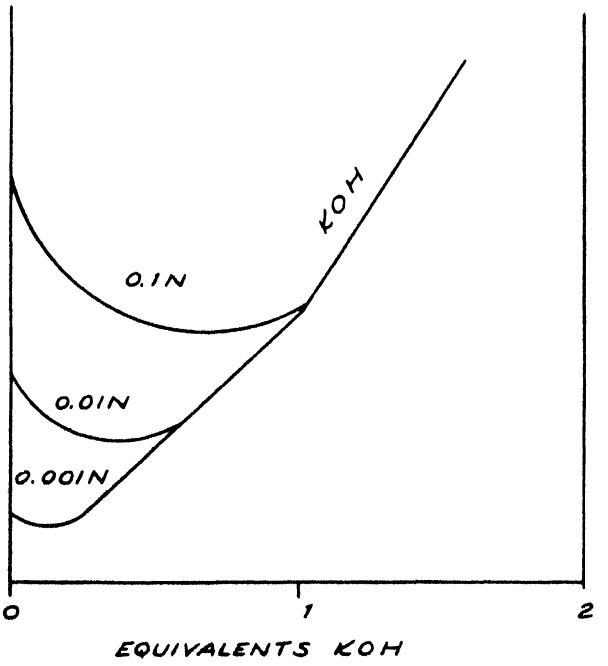

Fig. XIV-10a. Effect of concentration upon the conductometric titration curve of a weak acid with a strong base

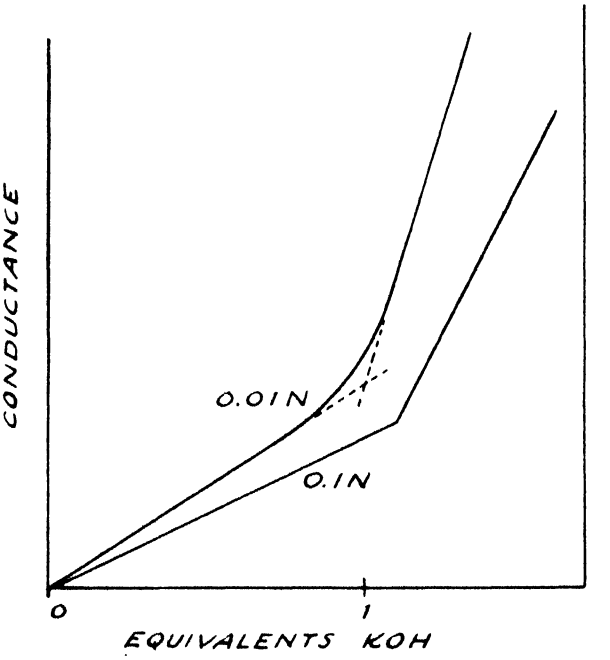

Fig. XIV-11. Titration curve of a very weak acid with a strong base

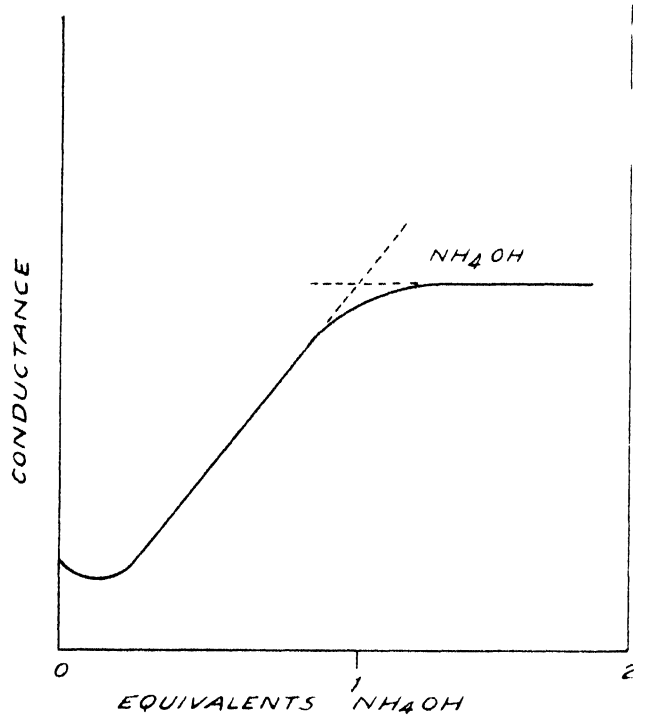

Fig. XIV-12. Titration of a weak acid with a weak base such as NH_4OH

conductance falls due to the replacement of ammonium ion by sodium, and, when this is complete, the conductance abruptly increases. Therefore, the sodium hydroxide is equivalent to the total acid present regardless of its preliminary partial neutralization by the ammonium hydroxide. A curve similar to Fig. XIV-14 will be obtained. These procedures are not suitable for very weak acids because of the strong hydrolysis when ammonium hydroxide is the titrating agent.

The conductometric method is very useful for the determination of equivalent weights of organic acids or bases, particularly amino acids and polypeptides. It has been applied to the titration of hydroxybenzenes, phenols, weak acids whose salts are colored, alkaloids, sulfonephthalein dyes, and amines. The method can be advantageously applied in the titration of mixtures of a strong acid and a weak acid. The potentiometric and visual methods are rarely adaptable to this problem.

The conductance curve, Fig. XIV-15, is actually a combination of the individual cases already discussed. The first break corresponds to the equivalence point for the neutralization of the strong acid, and the second break corresponds to the one for the weak acid. Practical applications include the determination of mineral acids in vinegar or other weak organic acids,

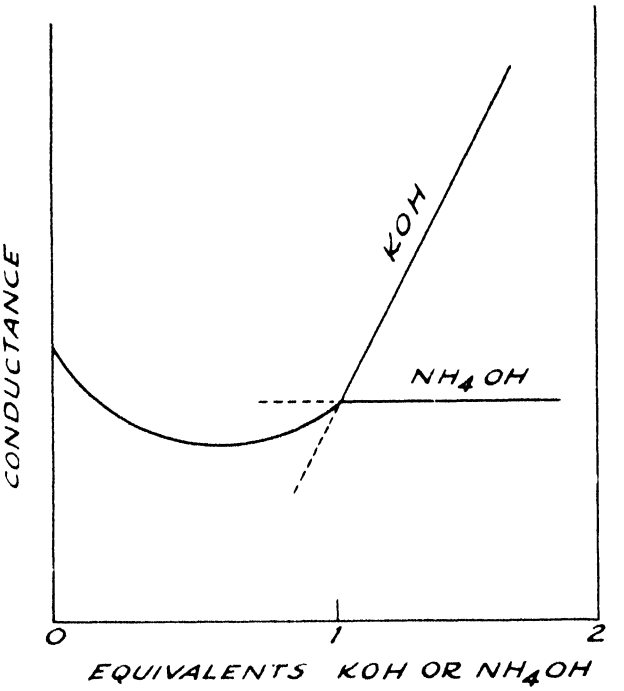

Fig. XIV-13. Titration of identical portions of sample with first KOH and then NH_4OH to locate the endpoint

and the titration of sulfonic acid groups followed by the phenolic groups in organic compounds.

Another type of reaction in which the conductometric method excels is the replacement titration of a salt of a weak acid or base, Fig. XIV-16. The indicator or potentiometric methods do not yield successful results when the acid or base is moderately weak, but as long as the ionization constant of the displaced acid or base divided by the original salt concentration does not exceed about 5×10^{-3}, the salt can be titrated accurately conductometrically. The method is particularly applicable for the determination of ammonia in fertilizer, and organic acid salts such as acetates, benzoates, succinates, etc. Addition of ethyl alcohol often enables salts of stronger acids or bases to be evaluated

Precipitation and Complex Formation Reactions. A precipitation or complex formation reaction can be made the basis of a conductometric titration if the following conditions are considered: (1) A slow rate of precipitation, especially with microcrystalline precipitates, prolongs the time of titration. Seeding or addition of alcohol is helpful. (2) Solubility of the precipitate or dissociation of a complex should be less than 5%. The former effect is alleviated by the presence of alcohol. (3) Adsorption or occlusion errors prevent constant composition of the precipitate.

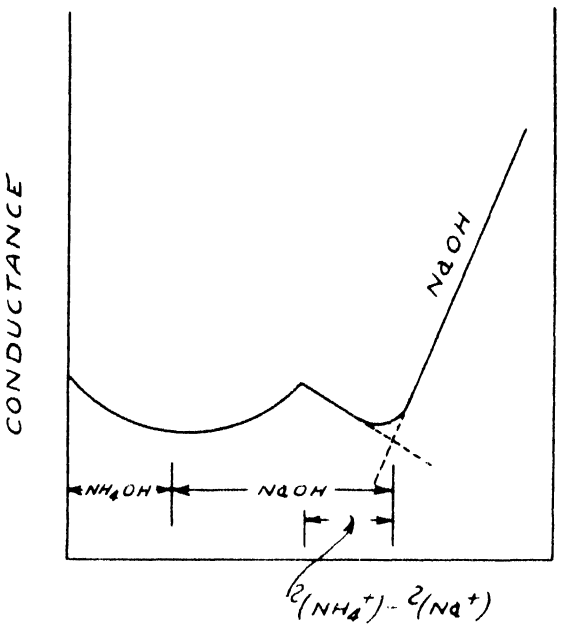

Fig. XIV-14. Partial neutralization of a weak acid with NH_4OH and then completion of the titration with NaOH of same concentration as NH_4OH

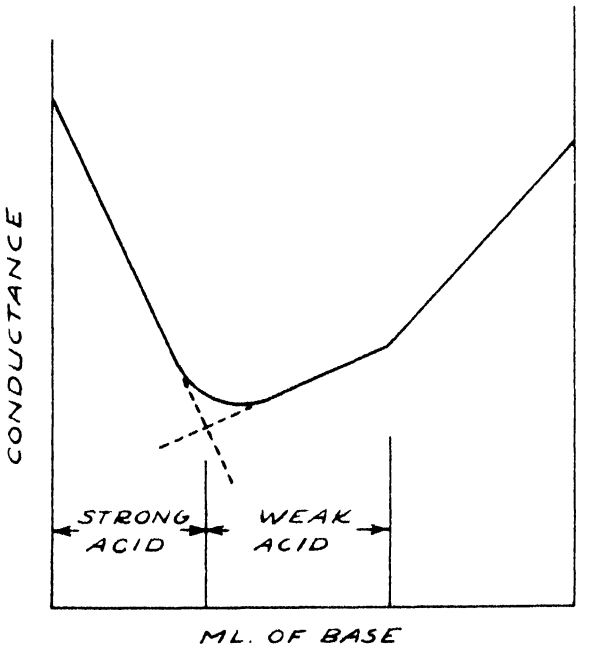

Fig. XIV-15. Titration of a mixture of a strong acid and a weak acid with a strong base

Even in favorable cases, results tend to be less accurate than in other reactions discussed. More so than in other types of conductometric

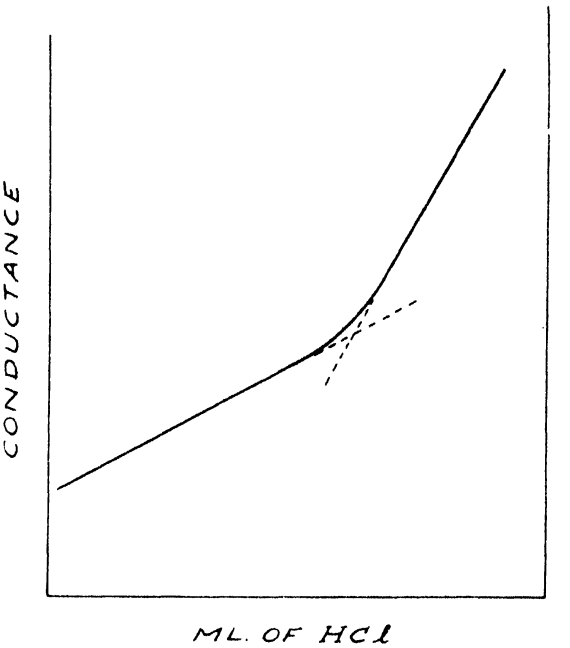

Fig. XIV-16. Typical replacement titration. Sodium acetate titrated with hydrochloric acid

titrations, ions should be selected that give as acute a conductance angle as possible, since freedom from the deleterious conditions enumerated above is somewhat dependent upon the acuteness of this angle. However, this is a difficult problem in precipitation or complex formation work. The precipitant should contain not only an ion which will produce the most insoluble salt or most stable complex, but also adhere to the following rules enunciated by Kolthoff[3]: (1) The smaller the mobility of the ion which replaces the reacting ion, the more accurate will be the result. (2) The larger the mobility of the anion of the reagent which reacts with the cation to be determined, or vice versa, the more acute is the angle. (3) The titration of a slightly ionized salt does not give good results, since the conductivity increases continuously from the beginning.

For these reasons, an acetate salt is preferable when titrating an anion, and a lithium salt when titrating a cation, Figs. XIV-1a and XIV-1b. On account of the solubility or dissociation factor, experimental data for plotting the conductance curves should be secured considerably removed from the equivalence point of the titration.

A considerable number of precipitation and complex formation reactions have been tabulated

3. Kolthoff, I. M., Ind. Eng Chem., Anal. Ed., 2, 229 (1930).

in the monograph by Kolthoff and Laitinen[4]. Literature references are included. Silver nitrate, lead nitrate, barium acetate, and lithium oxalate have received the most use in precipitation reactions, whereas mercuric perchlorate has found use as a reagent for complex formation reactions.

LABORATORY DIRECTIONS FOR CONDUCTOMETRIC TITRATIONS

General Instructions for the Operation of the Industrial Instrument Conductivity Bridge (adapted from the instruction book furnished by Industrial Instruments, Inc.)

1. Plug the cord of the instrument into a 110 volt, A.C. outlet. Snap the toggle switch to the On position, and allow 1 minute for the tubes to heat up.

2. Connect leads 1 and 2 of the bridge to the conductivity cell, see Fig. XIV-5. Use a cell with small electrodes far apart for solutions with low resistance and a cell with large electrodes close together for high-resistance solutions. Platinizing the electrodes sometimes allows sharper balancing of the bridge. Connect a decade capacitance box to terminals 2 and 3.

3. Place a volume of unknown solution, equivalent to 5 ml. of titrating agent, into the conductivity cell. Dilute the unknown solution until the electrodes are covered by at least 1 cm. depth of solution.

4. Set the multiplier switch at ".01" and rotate the main dial control the full length of its scale. If the "magic eye" indicator does not show a shadow angle, indicating a balance point, repeat the same procedure with the multiplier switch at positions ".1," "1," "10," and "100" successively until null indication is obtained at a readable point on the dial control scale.

5. Rotate the dial control in the direction which increases the size of the dark segment in the null indicator. At the balance point, the dark segment of the null indicator will show approximately a 90° maximum. If balance is obtained at a dial reading of less than 200, turn the multiplier switch to the next lower position and rotate the dial control in a clockwise direction until balance is obtained. Likewise, if the initial balance is obtained at a dial reading of more than 2000, turn the multiplier switch to the next higher position and rotate the dial control in a counterclockwise direction to obtain balance.

4. Kolthoff, I. M., and Laitinen, H. A., "pH and Electro Titrations," 2nd Ed., John Wiley & Sons, Inc., New York, 1941.

6. If a sharp balance is not obtained, use the decade condenser box across terminals 2 and 3. Obtain the best balance possible in the usual manner, then add capacitance from the box until the indicator shows the largest dark segment. Then readjust the dial control for best balance. This is repeated until further change of the dial control or capacitance setting results in a closing of the "eye" segment.

7. The resistance of the electrolytic cell in ohms is obtained by multiplying the dial reading by the value of the multiplier switch setting.

8. Place the titrating reagent in a 10 ml. microburet. Add successive portions of the titrating solution in approximately 0.5 ml. increments. Shake or stir the solution well after each addition. Allow the solution to become relatively quiescent and then measure the resistance as described above.

9. Continue the addition of titrating agent until four or more readings beyond the equivalence point have been obtained.

10. Plot the conductance of the solution in reciprocal ohms as the ordinate against the volume of titrating solution added as the abscissa. Extrapolate the two straight portions of the curve until they intersect, which corresponds to the equivalence point of the titration. If the plots exhibit a consistent deviation from linearity, multiply all resistance readings by the ratio, total volume/initial volume. Hand in the curves and the results.

General Instructions for Assembly and Operation of a Conductivity Bridge using an A.C. Galvanometer

1. The apparatus consists of the follow- pieces of equipment: An A.C. galvanometer, a Wheatstone bridge box, a conductivity cell, and a decade capacitance box.

2. Connect the terminals of the Wheatstone bridge box marked "BA" to the 6 volt terminals of the A.C. galvanometer. The galvanometer contains a 110 to 3, 6, or 9 volt potential divider to supply 60 cycle current for the bridge. The proper voltage is found by experience. In general, higher resistances require larger voltages in order to supply sufficient current for suitable galvanometer response.

3. Connect both terminals of the Wheatstone bridge box marked "GA" to the corresponding terminal on the galvanometer. Connect the electrodes of the conductivity cell to the terminals marked "X-1" and "X-2" on the Wheatstone bridge.

4. A Kohlrausch slide wire bridge, high resistance and decade resistance box, and a tapping key can be substituted for the Wheatstone bridge box. If this is done, connect,

as in Fig. XIV-4, the terminals of the slide wire marked "A" and "B" to the 6 volt terminal of the A.C. galvanometer. Connect the center tap of the slide wire "C" to the tapping key, in turn connected to galvanometer, "GA."

The electrodes of the conductivity cell are connected to "A" and to the remaining galvanometer lead, "GA." Also connected to the same galvanometer lead is the high resistance. In series with the high resistance is a decade resistance, whose other lead is connected to terminal "B" of the slide wire.

If the resistance changes are expected to be very small, insert the end coils by transferring the terminal connections at "A" and "B" to "A'" and "B'."

5. Connect the plug on the flexible lead of the galvanometer to a 110 volt, 60 cycle line, and release the galvanometer pointer from its clamp.

6. Zero adjustments:

(a) Mechanical: With the plug disconnected from the 110 volt line, release the pointer clamp of the galvanometer by moving the clamp button toward the scale as far as it will go. If the pointer does not come to rest at the zero point on the scale, turn the small molded disc at the top of the galvanometer until it does.

(b) Magnetic: Connect the plug on the flexible lead to a 110 volt, 60 cycle line. The measuring circuit leads should be connected to the galvanometer posts, and the tapping key on the bridge closed, but the low voltage leads from the galvanometer to the measuring circuit should be removed. If the pointer does not come to rest at the zero point on its scale, turn the thumbscrew in the center of the plate to correct this. When this adjustment is completed, the mechanical and magnetic zero points should coincide.

Replace the low-voltage leads to the measuring circuit, and the galvanometer is ready for use. When the experiment has been completed, the pointer should be clamped.

6. Place the solution to be titrated into the conductivity cell. Use a cell with small electrodes if the solution has a low resistance, and large electrodes for solutions with high resistance. Dilute the solution so that the electrodes are covered to a depth of 1 cm. or more.

7. Lock the "BA" push button on the Wheatstone bridge in the down or On position to turn on the current to the bridge.

8. Turn the ratio knob to 1 and balance the bridge by turning the resistance dials as needed. The galvanometer button "GA" or the tapping key is tapped each time adjustment has been made and the swing of the galvanometer is noted.

If the slide wire bridge is used, the decade resistance box is adjusted until balance can be obtained on some portion of the slide wire scale, preferably near the center of the scale.

9. Continue as described under section 6 and the remainder of the sections of the preceding general instructions.

General Experiments

A. Titration of a strong acid with a strong base. The effect of concentration.

Place 50 ml. of 0.01 N hydrochloric acid into the conductometric cell and measure its resistance. Then add successive portions of 0.1 N sodium hydroxide in 0.5 ml. increments. Measure the resistance after each addition.

Repeat the experiment using, first, 50 ml. of 0.001 N acid, then 50 ml. of 0.0001 N acid, and the necessary strengths of sodium hydroxide, 0.01 N and 0.001 N respectively.

B. Titration of a weak acid with a strong base.

Place 50 ml. of 0.1 N acetic acid into the conductometric cell and measure its resistance. Then add successive portions of 1.0 N sodium hydroxide in 0.5 ml. increments and measure the resistance after each addition.

Repeat the experiment using 50 ml. of 0.001 acetic acid. Titrate with 0.01 N sodium hydroxide.

C. Titration of a tribasic acid with a strong base.

Place 50 ml. of 0.05 M phosphoric acid into the conductometric cell and titrate with 2.0 N sodium hydroxide added in 0.20 ml. increments. The third inflection point is not distinct but can be obtained, with care, only if concentrated solutions are used - for example, at least 0.05 M acid and 2-4 M sodium hydroxide.

D. Titration of a very weak acid with a strong base.

Place 50 ml. of 0.1 N boric acid into the conductivity cell and titrate with 1.0 N sodium hydroxide added in 0.5 ml. increments.

E. Titration of an acid with a strong base, then a weak base.

Place 50 ml. of 0.2 N oxalic acid into the conductometric cell, and titrate with 1.0 N sodium hydroxide added in 0.5 ml. increments. Repeat the titration with an equal portion of oxalic acid, adding 1.0 N ammonium hydroxide in 0.5 ml. increments. The second inflection point will be much sharper when a weak base is used to titrate a weak acid; in this instance, the second replace-

able hydrogen of oxalic acid corresponds to a weak acid.

F. Partial neutralization of a weak acid with ammonium hydroxide and completion of the titration with a strong base.

The second method suggested by Righellato and Davies[2] to sharpen the end point in the titration of a weak acid will be carried out in the following experiment. Place 50 ml. of 0.1 N acetic acid into the conductometric cell and add approximately 4.0 ml. of 1.0 N ammonium hydroxide in 0.5 ml. increments. Complete the titration in the usual manner with 1.0 N sodium hydroxide added in 0.5 ml. increments. The volume of sodium hydroxide added corresponds to the original amount of acid present if the normality of the two bases are equal.

G. Titration of a mixture of a strong acid and a weak acid with a strong base.

Place 40 ml. of 0.1 N acetic acid and 10 ml. of 0.1 N hydrochloric acid into a conductivity cell, and titrate with 1.0 N sodium hydroxide, added in 0.2 ml. increments. This illustrates the method employed to determine the concentration of mineral acids present in weak organic acids.

Repeat the titrations using 20 ml. of 0.1 N hydrochloric acid and the same amount of acetic acid.

H. Replacement titrations.

Place 50 ml. of 0.1 solution of a salt of a weak acid or base into the conductometric cell, and titrate with either 1 N sodium hydroxide or hydrochloric acid, respectively. Add the titrating solution in 0.5 ml. increments. Suitable salts include the following: Any ammonium salt of a strong acid, hydroxylamine salts, hydrazine salts; acetates and nitrites of strong bases.

I. Precipitation titrations. The effect of suitable ions.

Place 5 ml. of a 0.05 N solution of silver nitrate into the conductometric cell, dilute with distilled water until the electrodes are completely covered, and titrate with a 0.1 N solution of potassium chloride. Repeat the titration, titrating with a 0.1 N solution of lithium chloride. Note the angle between the two branches of the conductance curve in each case, and consequently the effect of choosing a suitable cation in precipitation reactions involving the anion of the titrating agent.

The experiment might be repeated by titrating a solution of potassium chloride first with silver nitrate, and then with silver acetate to illustrate the effect of choosing suitable anions in precipitation reactions involving the cation of the titrating agent.

Place 10 ml. of a 0.01 M solution of a ferric salt into the conductometric cell, dilute with distilled water until the electrodes are more than completely covered, and titrate with a standard cupferron solution which has been standardized against electrolytic iron within three days of use. The cupferron solution is prepared by dissolving 30 g. of reagent quality salt in 500 ml. of water and storing in a dark bottle. Iron must always be oxidized with either bromine water or Superoxol to the ferric state prior to the titration, and the excess oxidizing agent removed by boiling for a short period.

Other suitable precipitation systems include cupric ammine acetate with alpha-benzoinoxime or salicyldoxime; sodium oxalate, molybdate, sulfite, or tungstate with lead acetate; and bismuthyl perchlorate with disodium hydrogen phosphate, pyrogallol, or lithium chloride.

J. Complex formation titrations.

Place 5 ml. of 0.1 N potassium iodide into the conductometric cell and titrate with a 0.1 N solution of mercuric perchlorate. A small break will occur at 1/4 mole mercuric perchlorate per mole of potassium iodide due to the formation of the complex salt, K_2HgI_4, after which the reaction

$$K_2Hg\ I_4 + Hg(ClO_4)_2 \rightarrow 2\ HgI_2 + 2\ KClO_4$$

will proceed until the stoichiometric proportion of 1/2 mole mercuric perchlorate to 1 mole potassium iodide is reached. Then the conductivity will increase sharply. Mercuric perchlorate may be prepared by saturating a known perchloric acid solution with the red mercuric oxide. The following alkali salts may be substituted for the iodide: Chloride, bromide, and thiocyanate.

SELECTED REFERENCES

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2. Jander, G. and Pfundt, O., "Leitfahigkeitstitrationen," Vol. II of Böttger, W. (Ed.), "Physikalische Methoden der Analytischen Chemie," Akademische Verlag., Leipzig, 1936.
3. Kolthoff, I. M., Ind. Eng. Chem., Anal. Ed., 2, 201, (1930).
4. Kolthoff, I. M., and H. A. Laitinen, "pH and Electrotitrations," 2nd Edition, John Wiley & Sons, Inc., New York, 1941.

CHAPTER XV

ELECTROLYTIC SEPARATION OF METALS

GENERAL PRINCIPLES

Electrolytic Cells

A cell may be defined as an arrangement of two electrodes and one or more solutions of electrolytes in a suitable container. If the arrangement is capable of furnishing electrical energy to some external system, it is called a voltaic cell. An example is the discharge cycle of the familiar lead storage battery. If, on the other hand, electrical energy is supplied from some external source and causes a current of electricity to flow through the cell, the arrangement is called an electrolytic cell. It is this latter form of cell to which our attention will be devoted in this chapter.

Single Electrode Potentials

When any solid or liquid chemical element is placed in contact with a solution of its ions, a potential is developed at the interface between the element and the solution. If the element is a gas, the potential between element and ion may be observed with the aid of a strip of unattacked metal, for example, Pt, Au. The magnitude of the potential appears to depend upon the relative tendencies of the ions of the element to leave the electrode, electrolytic solution pressure, and the opposing tendency, which is proportional to the osmotic pressure and hence to the activity of the ions of the element in the solution. Depending upon the nature of the element and the activity of its ions, the potential at the interface may be positive, zero, or negative. A copper rod dipping into a solution of copper sulfate (1 M) appears to have a double layer such that the copper rod is positive relative to the solution as indicated in Fig. XV-1a. The deposited copper ions form the positive part of the double layer. In Fig. XV-1b is illustrated a double layer in which the rod of metal is negative; this is due to the relatively great tendency of ions of active metals, for example, Zn, Mg, etc., to enter the ionic state. In this case the negative layer consists presumably of excess of electrons remaining when the layer of zinc ions splits off to form the positive part of the double layer. This double

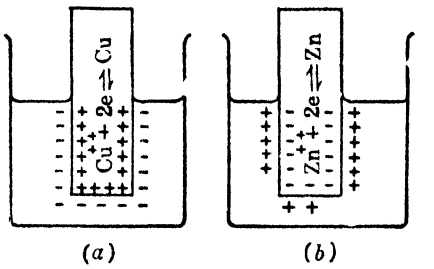

Fig. XV-1. Electrolyte double layers. (a) Copper in contact with a solution molar in cupric sulfate. (b) Zinc in contact with molar zinc sulfate

layer constitutes the electrode potential and the residual charge left on the electrode determines the sign of the electrode potential. On this basis the elements may be arranged in a table according to their single electrode potentials.[1] Such an arrangement of the elements is given in Table I of the Appendix. The single electrode potential under the special condition of unit ion activity is called the standard electrode potential and is commonly represented by E^{O}. Since these potentials are all relative, any one may be selected for reference and given the value zero; the normal hydrogen electrode is the one generally so selected.

Concentration Polarization

The term "polarization" has been often misused and, even when properly applied, has proved a source of confusion to the student. It can be defined as any change produced at an electrode by electrolysis or by some other means which causes the single electrode potential to differ from the normal or reversible value.

The potential of an electrode depends upon the difference between the electrolytic solution pressure of the material of the electrodes and the osmotic pressure of the ions of the electrode material. The change in electrode potential with ion concentration is given by a formula originally proposed by Nernst:

$$E = \frac{0.0591}{n} \log \frac{C_1}{C_2} \quad \text{at } 25^{O}\text{C.} \qquad (1)$$

where n is the valence of the ion involved, and

1. The signs of the single electrode potentials used in this book follow the convention adopted by the Foreign and American Electrochemical Societies.

C_1 and C_2 are the two ion concentrations, or, strictly, activities. If one of these concentrations is taken as unity (standard conditions), then the equation becomes at 25° C:

$$E = E^{o} + \frac{0.0591}{n} \log C \qquad (2)$$

Concentration polarization results when the concentration of ions in the immediate zone around the electrode is depleted due to electrolysis. The apparent electrode potential will then be different from that calculated using the concentration in the bulk of the solution.

Decomposition Potentials

If a certain small e.m.f. is applied to an electrolytic cell, only a very minute current passes, and no electrolysis occurs. If this potential is gradually increased, there will be only a slight increase in the current, until at some point electrolysis begins and the current increases rapidly. This is shown graphically in Fig. XV-2. The particular values, a and a', represented by the breaks in the current potential curves, are the decomposition potentials of the cathode and anode, respectively. At lower potentials than these no visible action has taken place at either electrode; above this value material is continuously set free at both electrodes. The small current which flows through the cell before the decomposition potential is called the residual current.

Various ions differ in the ease with which they exchange electrons. At the beginning of an electrolysis of a solution between two unattackable electrodes, the counter e.m.f. due to concentration polarization is zero. In order for electrolysis to begin, the applied e.m.f. would only need to be sufficient to overcome the resistance of the solution and to equal the decomposition potential of the materials undergoing electron exchange at the electrode surfaces. The decomposition potentials would have the same values as those given in the table of standard electrode potentials if the activity of the ion were unity and the overvoltage were zero.

To determine the individual decomposition potentials for a particular ion, it is only necessary to connect each electrode individually through a potentiometer with a standard reference electrode instead of measuring the voltage across the entire cell. The variation of a single electrode potential with current would be depicted either by the right or left-hand side of the curve shown in Fig. XV-2, depending on whether the electrode under observation were the cathode or anode.

The decomposition potentials of sulfuric, nitric, perchloric, phosphoric, and most organic acids,

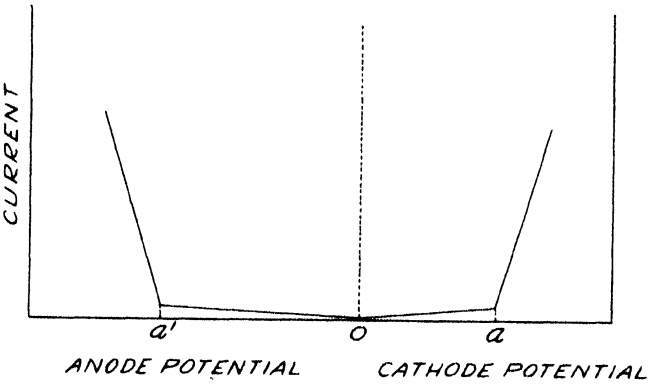

Fig. XV-2. Decomposition potential. The discontinuities (a) and (a') mark the beginning of the separation of the cathodic and anodic products of electrolysis, respectively, in substantial amounts

as well as many bases, possess nearly the same value, which leads to the natural conclusion that the electrode reaction in all cases must involve the same ions. The only reaction common to all the systems would be the discharge of hydrogen ions at the cathode and hydroxyl ions at the anode. Thus it appears that, although current is carried by all the ions present in the solution, those ions are not necessarily discharged, rather only those ions undergo electrode reaction whose decomposition potentials equal the existing electrode potential. In general, each ionic species will undergo electrode reaction as the appropriate potential is reached. This means that cations most readily discharged are those most noble, that is, have the most positive value of electrode potential according to the conventions adopted in this text. The process taking place at the anode will always be oxidation, so that anions with lower oxidation potentials will be discharged first.

For solutions of metallic salts, the decomposition voltage depends primarily upon the nature of the metal and little upon the nature of the anion, provided oxygen is the sole product liberated at the anode. For equivalent solutions of cadmium nitrate and cadmium sulfate, the values are respectively 1.98 and 2.03 volts; cadmium chloride, however, has a lower value, 1.88 volts, the anode process involving liberation of chlorine.

Overvoltage

It is evident from what has been said above that every ionic material requires a certain potential to cause it to discharge on the electrode. Theoretically this potential should be the same as the potential which an electrode of the ma-

terial being deposited would show in the same solution. It usually happens, however, that the material does not start depositing at this theoretical value, but at a higher one. This difference in potential between the theoretical value at which an ion should be discharged and the potential at which it actually is discharged is called an overvoltage.

Metals show small overvoltage effects in general. For the deposition of copper on a copper surface at low current densities the overvoltage is about 0.05 volt; but for higher current densities it may amount to several tenths of a volt. Oxygen shows an overvoltage of 0.4 volt at the anode in acid solution on smooth platinum, with low current densities.

For a reversible electrolytic process involving the discharge of hydrogen ions at the cathode and the liberation of oxygen at the anode, it can be calculated from the individual single electrode potentials that the decompostion voltage should be about 1.2 volts. As was pointed out earlier, however, the decomposition potential is actually about 1.7 volts for most acids and many bases with smooth platinum electrodes. Although the value is constant, it is considerably different from 1.2 volts. Furthermore, the decomposition potential is different if other metals are employed as electrode materials. By measuring the separate potentials, using an auxiliary standard reference electrode, at cathode and anode, when hydrogen and oxygen, respectively, are being evolved, and subtracting the calculated reversible potentials for the same solution, the cathodic and anodic overvoltages can be determined.

Overvoltage depends upon several factors; one of the most important is the material being used as electrode. For instance, if the cathode is platinized platinum, the break in the cathode current curve would come at a value which is the same as a hydrogen electrode would show in this solution; in other words, hydrogen ions are discharged on a platinized platinum electrode at the theoretical potential. If another material is used, a greater potential than the theoretical must be applied before the hydrogen ions are discharged, and this difference is the overvoltage of hydrogen on this material. The overvoltage of hydrogen on a metal is a function of its position in the periodic system; the metals in each vertical group have approximately the same value, as shown in Table 1.

Another important factor that affects overvoltage is current density; an increase in current density always increases the overvoltage. Current density is the current per unit area of electrode surface. It is usually expressed as amperes per square centimeter. Fig. XV-3 represents the various cathodic decomposition potentials for hydrogen on the different electrodes. In this set of curves the decomposition potential is the potential value at which the curve starts in each case. The overvoltage is given by the actual value on the potential scale since the material being deposited is hydrogen and the zero on the potential axis is taken as the theoretical value for the hydrogen electrode in the solution used; or it is the value at which hydrogen is actually deposited on the platinized electrode. For any given material, the difference in the potential value at the point where the curve starts and the value at any given current density gives the overvoltage due to current density.

Temperature also affects overvoltage. An increase in temperature decreases the overvoltage.

TABLE 1. OVERVOLTAGE OF HYDROGEN IN VOLTS[2] ON SMOOTH ELECTRODES IMMERSED IN 2 N H_2SO_4 AT 25°C. AND A CURRENT DENSITY OF 0.01 AMP./CM.^{2}

Periodic Group	I B	II B	IV A	V A	VIII
	Cu 0.58 Ag 0.76 Au 0.39	Zn 0.75 Cd 1.13 Hg 1.04	C 0.70 Sn 1.08 Pb 1.09	Bi 1.05	Fe 0.56 Ni 0.40

2. Knobel, Caplan, and Eiseman, Trans. Am. Electrochem. Soc., 43, 55 (1923).

Laws of Electrolysis

Ohm's law states the relation between current, resistance, and potential, or e.m.f. It is usually expressed in the form

$$I = \frac{E}{R} \qquad (3)$$

where E is the electromotive force in volts; R is the resistance in ohms; and I is the current expressed in amperes. This law applies for all conductors, including electrolytes.

The relationship between the quantity of electricity passed through an electrolyte and the electrochemical changes taking place at the electrodes are expressed in two laws known as

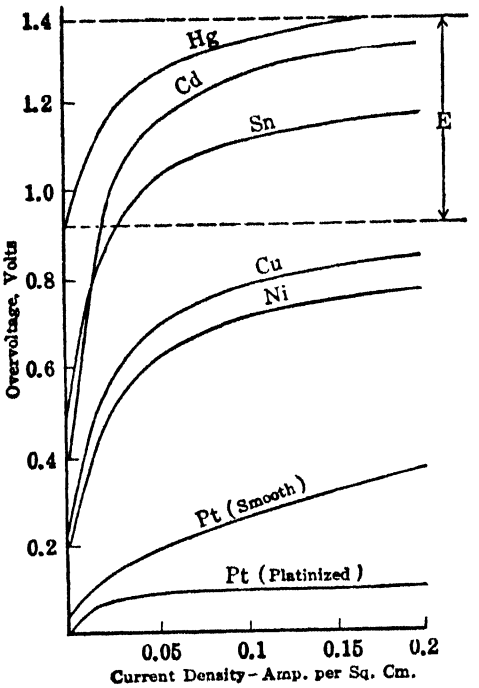

Fig. XV-3. Cathode over-voltage of hydrogen on various metal electrodes as a function of current density. Plotted from, data by Knobel, Caplan, and Eiseman, Trans. Am. Electrochem. Soc., 43, 55 (1923) and other sources

Faraday's laws of electrolysis. The laws are:

1. The quantity of a given substance which is liberated at an electrode is proportional to the quantity of electricity passed through the system.
2. The amounts of different substances which are deposited by the same quantity of electricity are proportional to the chemical equivalents of the substance.

ELECTROLYTIC SEPARATION METHODS

Conditions for Separation of Metals

In connection with the possibility of the electrolytic determination of a given metal it is always necessary to take into consideration the other ions present and the overvoltage to be expected. Suppose for instance the solution is 0.01 M with respect to silver and 1 M with respect to copper. The potential at which silver would start to deposit from such a solution is given by the equation

$$E = E^{o} + 0.0591 \log [Ag^{+}]$$
$$= 0.800 + \log (0.01) = 0.682 \text{ volt} \quad (4)$$

When silver has been reduced to a negligible value, say 10^{-7} M, the potential at the electrode surface is

$$E = 0.800 + 0.0591 \log 10^{-7} = 0.386 \text{ volt} \quad (5)$$

From the table of single electrode potentials it is observed that the potential of the copper electrode in a 1 M solution is 0.344 volts, which is more negative than the value of silver in the 10^{-7} M solution, which means that no copper would be deposited if we stopped the electrolysis at 0.386 volt.

A type of electrolytic separation of great practical importance is the determination of a metal in a neutral or acid solution. From a consideration of the standard electrode potentials it might be expected that separations in an acid solution would be limited to metals more positive than hydrogen; this, however, is by no means the case. It has already been pointed out that hydrogen starts to deposit at its theoretical value only on platinized platinum. For any other metal a more negative value is required. The magnitude of this negative value depends in a rather pronounced manner upon the metal used as cathode, the physical condition of the metal, the current density, and the temperature. Another point to be remembered is the influence of hydrogen-ion concentration on the hydrogen deposition potential. Even on a platinized platinum electrode, hydrogen would not start to deposit from a neutral aqueous solution until the electrode had a value of $E = 0.0591 \log 10^{-7}$, or -0.414 volt. Then, if the metal used as electrode possessed an appreciable hydrogen overvoltage, this value would also shift the deposition potential of hydrogen to a still more negative value. This means that metals, even as electronegative as zinc, can be completely separated from an alkaline solution due to the combination of decreasing the hydrogen-ion concentration and the high overvoltage of hydrogen upon a zinc electrode.

In general the conditions necessary for the satisfactory separation of a metal from one or more metals present in the solution may be summarized as follows:

1. An univalent cation can be completely separated from another if the deposition potential of the other cation from that particular solution is less noble, or more negative, than 0.35 volt. In the case of the separation of a bivalent metal the theoretical difference need be only about 0.2 volt. Of course, if the less noble cation is present to the extent of only a few milligrams, a much smaller difference may suffice.
2. The two metals must not form an exothermic

alloy or amalgam, since under these circumstances the potential of the metal is lowered to the more noble alloy electrode potential. Some metals do not form amalgams with mercury and may therefore be separated from those which do as will be discussed in a later section on the mercury cathode.

3. The metals may be separated at different electrodes. Certain metals - lead, manganese, and cobalt - may be deposited as higher oxides at the anode.

Character of the Deposit

The physical characteristics of the deposit on the electrode are generally more satisfactory when the substance is deposited from a solution containing complex rather than simple ions. A better deposit of silver is obtained from a silver cyanide solution than from a silver nitrate solution. For a similar reason depositions are often carried out in an ammoniacal medium. Complex salts have greater "throwing power," that is, give a better deposit in hollow surfaces. They also give a finer grained crystal deposit which obviates "tree growth." Protective colloids act similarly.

Simultaneous deposition of an excess of hydrogen together with a metal may cause the latter to separate in a spongy form, readily oxidized and loosened from the electrode. Spongy deposits are often caused by the metal existing primarily in the form of an unstable compound, generally the hydride, which is subsequently decomposed with evolution of gas. A typical instance is bismuth, which can be obtained in coherent form from many solutions if the cathode potential is sufficiently low to prevent hydride formation. The presence of oxidizing agents, for example, nitric or persulfuric acids, tends to prevent the formation of hydride, when the presence of these reagents can be tolerated, as in the copper deposition.

Heating to 80°-100°C. in many cases improves the purity and physical properties of the deposit. The effect is due in part to mechanical stirring and in part of changed ionization, conductance, and overvoltage effects.

Other things being equal, mechanical stirring often improves the character of the deposit. The outstanding advantage of stirring the solution is that a very high current density may be used without injuring the purity or physical character of the deposit. A great saving of time is possible since a liberal supply of metal ions is brought to the cathode, and the current is principally used in the deposition of metal. Without adequate stirring, the solution near the cathode may become impoverished in metal ions, with the result that the decomposition potential increases to the point where a second cation starts to deposit. If the second cation is hydrogen ion, the spongy deposits previously mentioned will result; if another metallic ion, contamination of the deposit will result. Stirring brings fresh ions up to the electrode and thus decreases concentration polarization.

Every dissolving substance has on its surface an infinitely thin layer of its saturated solution from which it diffuses into the surrounding medium. This layer can be kept very thin by stirring and the solution velocity will be proportional to the difference in concentration between the saturated solution and outer solution. The thickness of this layer varies with the velocity of stirring and the temperature and can be calculated to be 0.018 - 0.052 mm.

The process of depositing a metal is divided into three parts:

1. Diffusion of the substance toward the cathode.
2. Chemical reaction in the liquid phase.
3. Transition of the liquid into the solid phase (including the discharge of metal ions).

Process (1) is very slow; (3) is very rapid; (2) can, according to the nature of the reaction, be infinitely rapid, or have a measurable velocity, or be very slow. From simple salts, metal ions are supplied with infinite rapidity, from complex salts with a finite velocity, very great but measurable. To the very slow class belong many organic reactions.

Of the three processes stirring will primarily hasten only diffusion, but this will influence the second process, - the ionic reactions. It is a general law that the influence of stirring ceases when the velocity with which the solution is renewed attains the velocity of the reactions occurring in the solution. If the latter is infinitely great, then there is no limit to the effect of increasing the velocity of stirring. If, on the other hand, the reaction velocity is limited, as with complex salts, the effect of stirring in hastening the deposition of metal soon reaches its limit. The thinner the diffusion layer, the greater the reaction velocity; and, to make the layer thinner, more rapid stirring is required. Stirring, as has already been mentioned, by increasing somewhat the average concentration in the layer adhering to the cathode, lowers the concentration polarization of the cathode usually 0.1 - 0.2 volt. Table 2 shows the effect of stirring and of other conditions on the deposition of copper from a

nitric acid solution. The influence of rate of stirring is considerable. A decrease in concentration of nitric acid has a slight effect. An increase in current density and temperature has some effect. The influence of stirring on the velocity of reduction in the case of complex salts must obviously be relatively slight because of the relative slowness of dissociation of complex ions into

TABLE 2. EFFECT OF VARIOUS FACTORS ON SPEED OF DEPOSITION OF COPPER

Volume HNO_3 ml.	Stirring Rate r.p.m.	Current in Amperes	Temperature (°C.)	Time in Minutes
22	0	1.0	20	310
20	800	1.0	20	62
20	800	2.0	20	60
12	800	1.0	20	60
2	800	1.0	20	58
20	1600	1.0	20	52
2	800	2.0	20	48
2	800	2.0	95	40
1	800	3.25	90	20

metal ions. In depositing copper from cyanide solution the increase is only 26%; from cupric ammonia solution, 61%; corresponding to the greater stability of the cyanide complex.

The influence of stirring on the separation of copper from zinc is instructive. At high speed even 4 amperes can be used without danger of zinc being deposited toward the end of the process. If the stirring rate is decreased, zinc will be deposited on the copper toward the end. Insufficient nitrate ions (whose reduction occurs readily) are supplied from the main body of the solution, and zinc is deposited in preference.

Neither the property of a deposit nor reaction velocity depends upon a movement of the electrode on which it is deposited. It makes no difference whether the anode or cathode is revolved, or whether they are kept stationary and an auxiliary stirrer is used. At high current densities and with poorly conducting electrolytes there is often a rise in potential caused by an increase in resistance between rotating electrode and solution. It can be avoided by putting a glass cross over the rotating electrode, thus causing the electrolyte to flow over it better.

Complex salts forming electronegative ions containing the metal are very favorably affected by stirring because the complex ion migrating away from the cathode is continually returned to it.

ELECTRODEPOSITION BY CONSTANT CURRENT METHOD

Apparatus. A diagram of apparatus for electroanalysis is shown in Fig. XV-4. The source

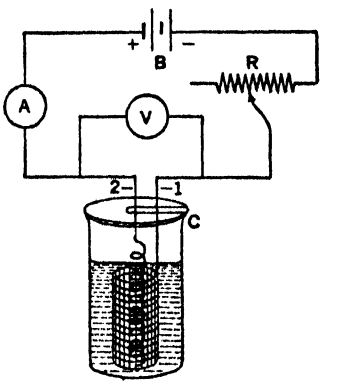

Fig. XV-4. Apparatus for electro-analysis by constant-current method. A, Ammeter; B, source of direct current; R, a variable resistance; V, voltmeter; 1, gauze electrode; 2, spiral anode; C, split watch glass

of direct current may be a storage battery or rectified alternating current. The electrode upon which the deposition takes place may be either a dish, cylinder, cone, or gauze of suitable material. In some cases it is desirable to use a mercury cathode. In addition provision should be made for introducing a stirrer or rotating one electrode, and for heating the solution during electrolysis. Several commercial, self-contained instruments are available; among these are the Sargent-Slomin electrolytic analyzer, Fig. XV-5; and the Wilkens-Anderson Company's apparatus, Fig. XV-6.

Electrodes are customarily constructed of 52, 48, or 45 mesh platinum gauze, since mesh of this size presents the largest surface consistent with adequate mechanical strength. Pure platinum is never used; rather an alloy of 90% platinum and 10% iridium or rhodium is usually used because it displays lower solubility characteristics and more rigidity.

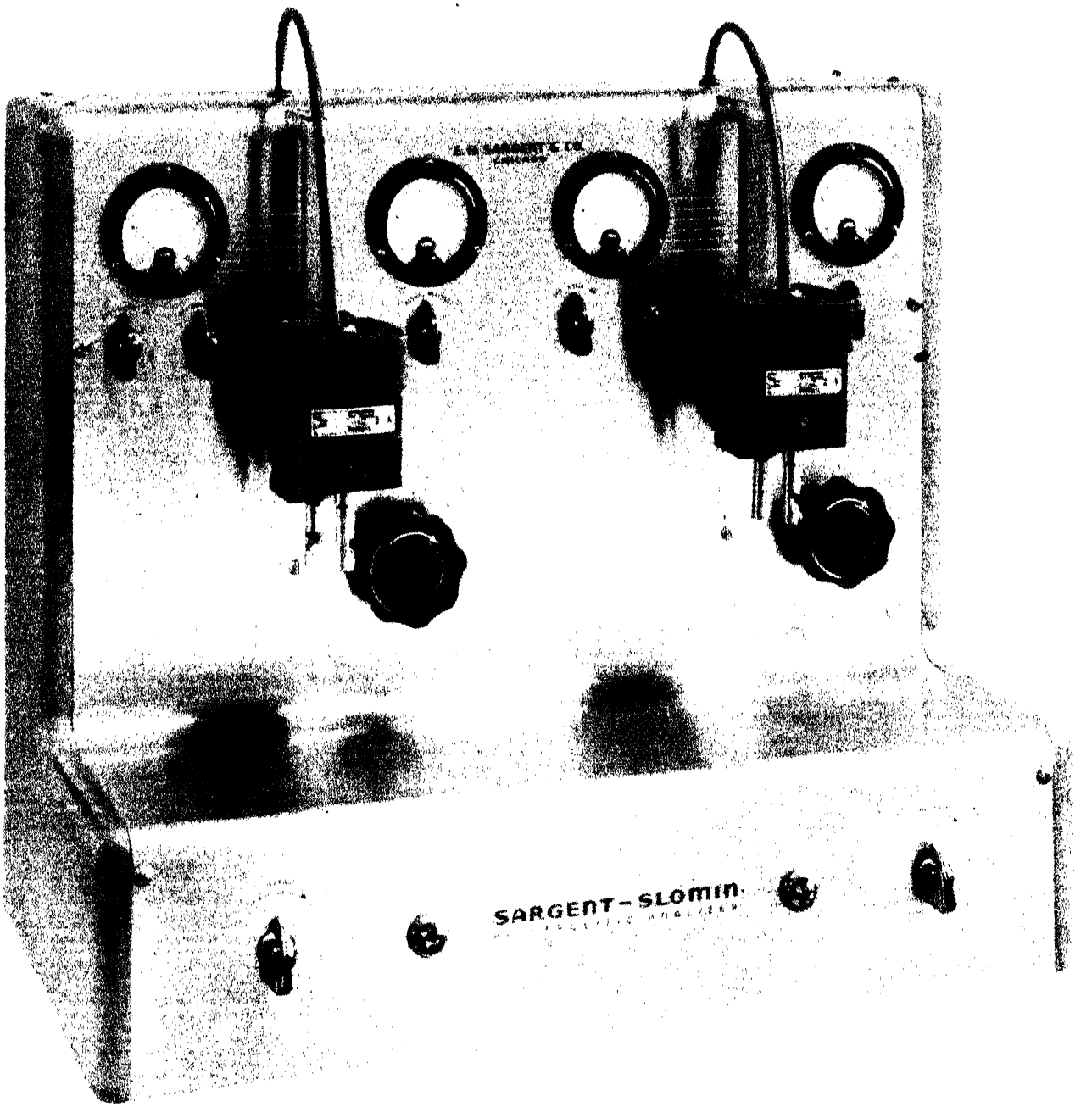

Fig. XV-5. The Sargent-Slomin Electrolytic Analyzer (Courtesy of E. H. Sargent and Company)

Electrolysis in Presence of Several Ions which Can Be Deposited

Hydrogen ions are always present in a solution, and therefore, the deposition of any cation always involves a separation of it from hydrogen. Likewise, the evolution or deposition of any anion involves the separation of it from oxygen derived from hydroxyl ions present in the solution. Since most interest is centered in the deposition of cations, only this class of separations will be discussed; however, the conditions for electroanalysis of anions are analogous.

Metals more noble than hydrogen may be separated from those less noble than hydrogen by proper regulation of the acidity of the electrolytic solution. If the cathode current density is maintained at a constant value, at first only the nobler metal is deposited, but as the concentration of nobler metal ions is reduced, the potential gradually rises until hydrogen is also liberated.

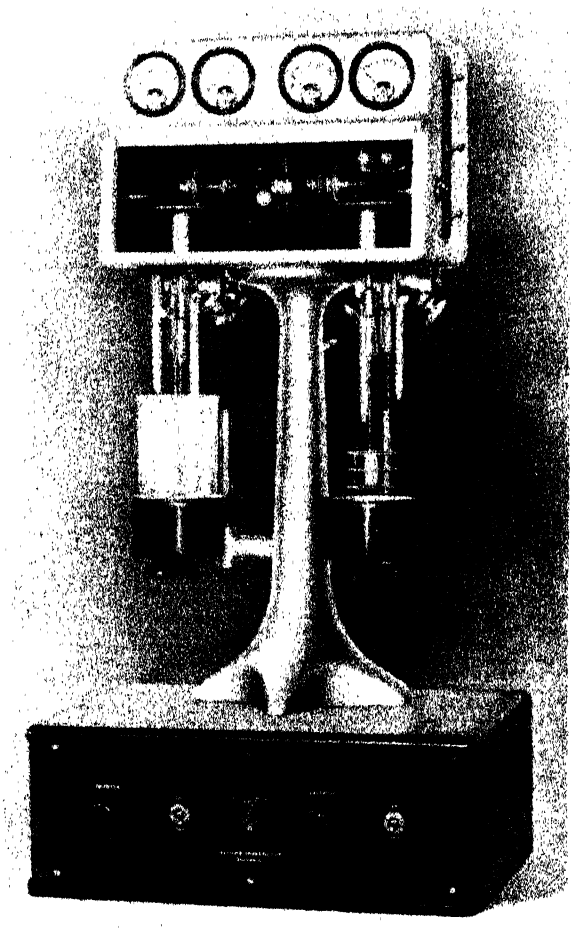

Fig. XV-6. The Waco Electrolytic Apparatus (Courtesy of the Wilkins-Anderson Company)

When hydrogen evolution is noticed, it can be assumed that the electrolysis of the nobler metal is essentially complete. This procedure is applicable even to metals whose electrode potentials are considerably less noble than that of hydrogen either by reducing the acidity of the solution and thereby shifting the decomposition potential of hydrogen to more negative values, or by taking advantage of the high overvoltage exhibited by hydrogen toward some electrode surfaces.

The constant current method usually will not provide a means for selectively depositing two or more metals more noble than hydrogen when they are present, together, in the same solution unless some chemical property of one or all of the cations is altered. If one of the cations is capable of forming a complex ion, or if the stability of the complex formed by the different cations is sufficiently different, it might be possible to deposit selectively one cation in the presence of the others. One characteristic of a complex salt is the very low concentration of metallic ion in equilibrium with the undissociated complex. Consequently, the decomposition potential becomes more negative for a complex ion than for a single cation, and can be made still more negative by increasing the concentration of the complexing agent. Table 3 illustrates these effects for some cyanide complexes. Cadmium and copper are striking examples illustrating the role played by complexing agents. The normal electrode potential of copper is over 0.7 volt more positive than that of cadmium; yet, in a 1 N potassium cyanide solution, the relative electrode potentials of the two metals are completely reversed, so completely that cadmium may be quantitatively separated from copper under these conditions. Similar possibilities for altering the normal order of electrodeposition exist in sulfide solutions of thiosalts and in ammoniacal solutions with ammine salts. Since these particular complexing agents require low hydrogen-ion concentration, the reversible decomposition potential for hydrogen is also shifted to more negative values.

Increase in temperature increases the conductivity of solutions and the diffusion coefficient of all ions, and decreases the viscosity of the solutions. Since simple ionic reactions proceed with infinitely great velocity, the velocity of electroreduction of a metal from its simple salt is not appreciably increased with rise in temperature. But the velocity with which metal ions are formed from a complex is finite and must, therefore,

TABLE 3. RELATION BETWEEN ELECTRODE POTENTIAL AND METAL CONCENTRATION FROM DISSOCIATION OF COMPLEX SALTS ACCORDING TO FOERSTER [3]

Electrolyte	1 N H_2SO_4	0.1 N Metal Cyanide Complex in All Cases		
		0.2 N KCN	0.4 N KCN	1.0 N KCN
Zn	- 0.76	- 1.03	- 1.18	- 1.23
Cd	- 0.40	- 0.71	- 0.87	- 0.94
Cu	+ 0.34	- 0.61	- 0.96	- 1.17

3. Foerster, Z. anorg. angew. Chem., 19, 1842 (1906).

like all chemical reactions, be accelerated with temperature; and the less dissociated the complex ion, the greater the effect. This relation for $Ni(NH_3)_4^{++}$ and $Cu(CN)_2^-$ is linear, and the effect especially marked in the latter case because of its great stability. In an ammoniacal solution the decomposition potential of the nickel ammine ion is greatly reduced, from -0.9 to -0.6 volt, by heating the solution from room temperature to 90°C., whereas the corresponding potential of the zinc ammine ion suffers only a slight change, from -1.14 to -1.05 volts. This change allows only nickel to be deposited at 90°C. whereas an alloy of the two metals would be obtained at room temperature. Similarly a separation of antimony from tin from a sulfide solution is based upon this temperature effect. Root [4] gives tables showing relative decomposition potentials for various complex electrolytes using platinum anodes.

The use of depolarizers sometimes renders a separation between two metals possible by maintaining the cathode potential below the limiting value. Oxidizing agents, such as the nitrate ion, act as depolarizers in cathodic reactions; and reducing agents, such as hydroxylamine or hydrazine, act as depolarizers in anodic reactions, being oxidized more easily than other substances.

ELECTRODEPOSITION BY CONSTANT POTENTIAL APPLIED TO ELECTRODE TERMINALS

A method of electrolytic separation has been devised which is based upon the application of a definite, constant potential to the electrodes of the electrolytic cell. This potential must be sufficient to overcome any ohmic resistance in the circuit or cell, and to exceed the decomposition potential of the metallic salt, stated symbolically thus:

$$E = (E_c + \omega_c) - (E_a + \omega_a) + IR \qquad (6)$$

in which E_c is the reversible, single electrode potential between the cathode and the solution; ω_c is the cathode polarization or overvoltage; E_a and ω_a are the corresponding terms at the anode; and IR is the potential drop between the cathode and the anode, R being the resistance of the electrolyte between the cathode and the anode. During an electrolysis the term $(E_a + \omega_a)$ remains about constant, the reaction at the anode usually being the evolution of oxygen and the conditions governing it being largely unchanged, although the chemical polarization term is dependent upon the current density.

Generally speaking, then, any significant changes in electrode potential will be confined to the cathode. If two competing reactions have electrode potentials sufficiently far apart to favor the complete reaction of the most noble system before the second competing reaction commences, it is only necessary to limit the total potential being applied to the cathode and anode to a value below that necessary to allow the second competing reaction to occur. The current decreases steadily during the electrolysis to a very small value. Stirring is necessary to shorten the time required for complete electrolysis.

Since the current is gradually changing, the chemical polarization effect observed at the anode will not remain constant; and, therefore, the term $(E_a + \omega_a)$ does not remain strictly constant. Furthermore, as the result of electrolysis the resistance of the solution between the anode and cathode is altered. Thus, a rigid control or limitation of the cathode potential is not possible so that metals situated close together in the electromotive series cannot be satisfactorily separated. This disadvantage is overcome in the limited cathode potential method.

LIMITED CATHODE POTENTIAL METHOD

In the normal practice of electroanalysis, the change in the cathode-anode voltage during the electrolysis is no clue to the extent of the deposition of a metallic ion, but is the algebraic difference of the voltages between the solution and the cathode and anode and the IR drop through the solution (equation 6), all of which may undergo change during the electrolysis. Consequently, as has been pointed out, possible separations by the constant current method are limited to those metals below hydrogen in the electromotive series from those above hydrogen, hydrogen being evolved after the deposition of the lower metal in preference to deposition of the higher metal. Both of the previously discussed methods fail if the second metal lies only slightly above the other in the electromotive series unless the decomposition potentials can be shifted through formation of a suitable complex ion or by other means.

By inserting a reference half-cell into the solution and measuring the voltage between the cathode and the reference cell, it becomes possible to isolate the effect at the cathode in the manner described for determining single electrode potentials in an earlier section. The voltage between the solution and the cathode consists of

4. Root, J. Phys. Chem., 7, 428 (1903).

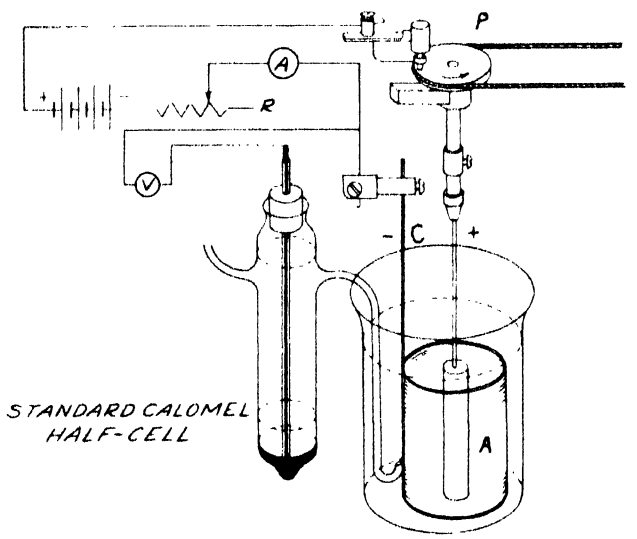

Fig. XV-7. Circuit and apparatus for limited cathode potential electrodeposition

the equilibrium voltage of the electrode metal toward the solution containing its ions, and concentration polarization caused by the flow of current, as given by the Nernst equation:

$$E = E^{o} + \frac{0.0591}{n} \log [M^{n+}] \qquad (7)$$

As the metal-ion concentration is decreased during the progress of electrolysis, the logarithmic term becomes progressively smaller, moving the cathode potential toward the negative end of the electromotive series. Every tenfold decrease in metal-ion concentration shifts the cathode potential 0.0591/n volt more negative. Thus there is provided a means of following the change in the concentration of a metal ion during the electrolysis and, by controlling the cathode potential, of effecting the separation of one metal from another lying somewhat higher in the electromotive series.

Apparatus. The circuit and apparatus required for limited cathode potential electrodeposition is shown in Fig. XV-7. The electrical potential applied to a cell to cause electrolysis is supplied by a lead storage battery, Ba, or from rectified alternating current; S.C. is the auxiliary reference electrode; A, a three-scale ammeter, 0 to 100, 1000, and 10,000 milliamperes; V, a vacuum-tube voltmeter or potentiometer; R, adjustable resistance capable of carrying up to 15 amperes; C, the platinum gauze cathode; A, the platinum gauze anode rotated by the pulley, P.

The potential between the cathode and the reference cell must be measured with an instrument which will draw little or no current from the reference cell. The total potential measured is equal to the difference between the reference half-cell and cathode potentials:

$$E_{\text{total pot.}} = E_{\text{ref.}} - (E_c + \omega_c) \qquad (8)$$

Since their inception by Sand,[5] limited cathode potential separations have not become popular, even though a number of very useful applications of the method have been devised. In the early work, the continuous attention of an operator was required throughout the entire electrolysis which usually consumed no less than 60 minutes, definitely a detracting feature. However, Diehl[6] and Lingane[7] have described two pieces of apparatus for automatically controlling the potential throughout the entire electrolysis. Diehl's apparatus is shown in Fig. XV-8.

Furthermore, recent work by Diehl and the authors has shown that the time for electrolysis may be materially shortened through the use of high current densities. Copper separations have been completed in less than 10 minutes using an initial current of 10-12 amperes and manual control. The relatively expensive automatic equipment is not necessary when the operator's attention is demanded only for such a short time. These recent advances warrant a reinvestigation of the possibilities of this method for routine analytical separations.

General Technique of Limited Cathode Potential Electrolysis

In order to prevent the cathode potential from exceeding a limiting value it is simply necessary to decrease the potential applied to the cathode and anode by increasing the resistance, R, shown in Fig. XV-7. In Fig. XV-9 are plotted the cathode-reference cell potential, E, and the electrolyzing current, I, against time for the deposition of copper from copper sulfate-sulfuric acid solution containing tin. The cathode potential becomes more negative rapidly at the beginning of the electrolysis as the platinum gauze is

5. Sand, H. J. S., J. Chem. Soc., 91, 373 (1907). Also "Gravimetric Electrolytic Analysis," Vol. II, Blackie and Son, London (1940).

6. Diehl, H., "Electrochemical Analysis with Graded Cathode Potential," G. F. Smith Chemical Co., Columbus, 1948. See also Caldwell, C. W., Parker, R. C. and Diehl, H., Ind. Eng. Chem., Anal. Ed., 16, 532 (1944).

7. Lingane, J. J., ibid., 17, 332 (1945).

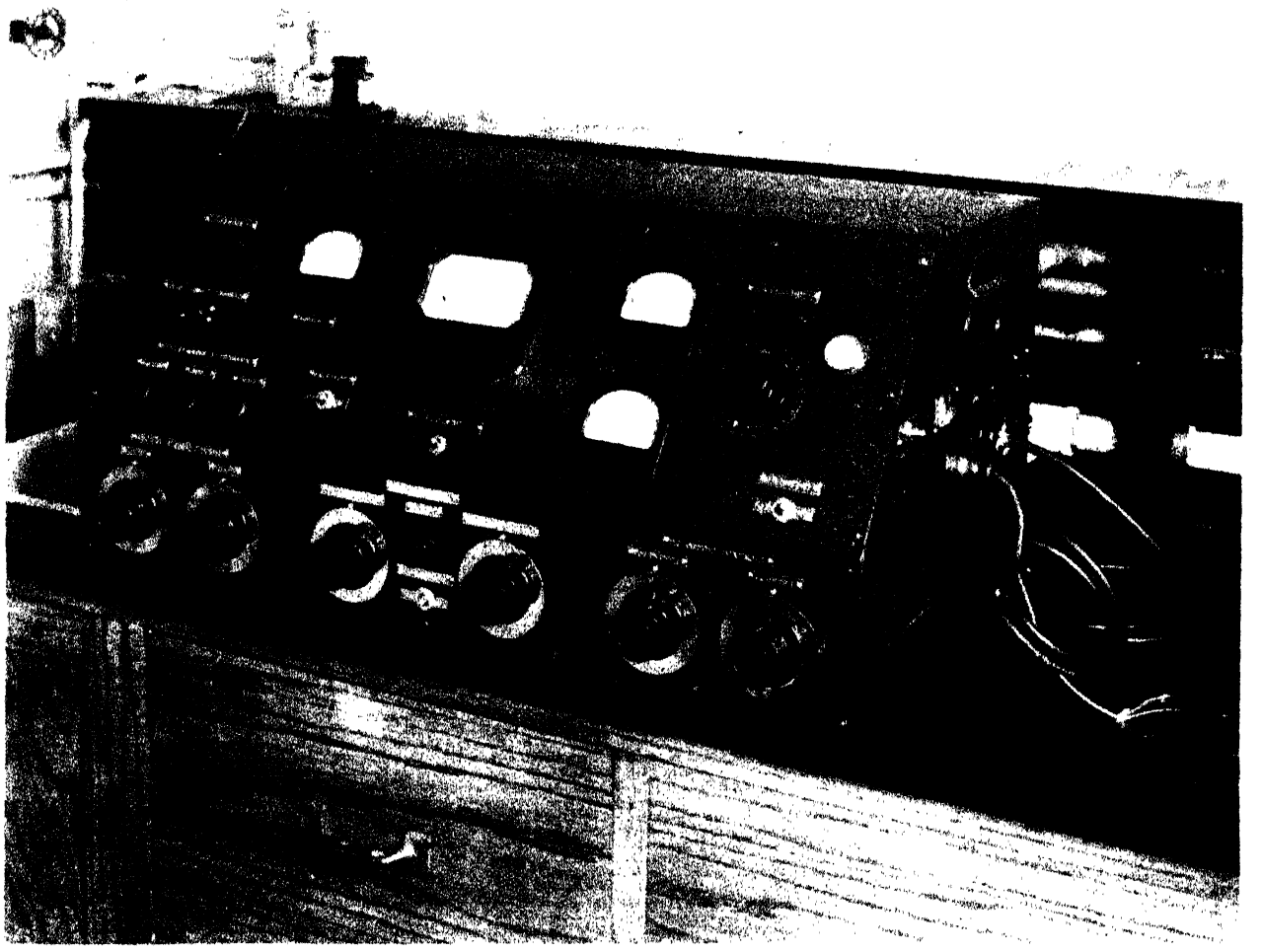

Fig. XV-8. Diehl's apparatus for automatic limited cathode potential electrodeposition (Courtesy of the G. Frederick Smith Chemical Co.)

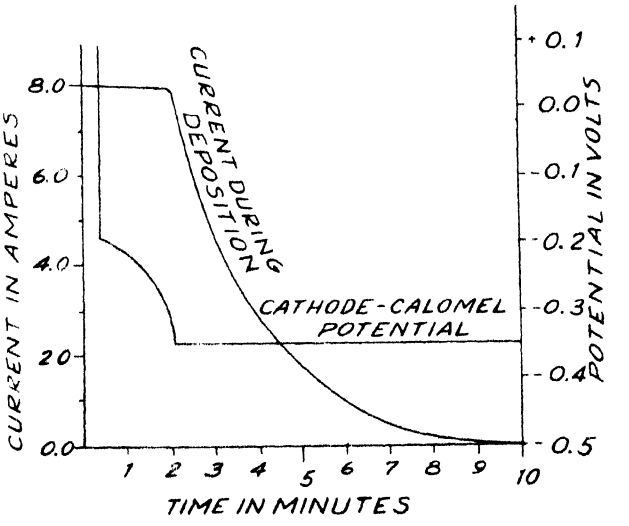

Fig. XV-9. Cathode-calomel potential and the current passing through electrolytic cell during deposition of copper by limited cathode potential method, from a hydrochloric acid solution

covered with copper and as the copper is deposited. Shortly afterward the current decreases as the resistance, R, is increased to prevent the cathode from becoming more negative than -0.35 volt toward the saturated calomel reference electrode. Ultimately the copper is all plated out and the electrolysis is completed, although the current never falls completely to zero as would be expected, probably due to a minor cyclic side-reaction.

It cannot be too strongly emphasized that rapid stirring or the rotation of the anode is very important for a successful separation. Fresh ions must constantly be brought to the electrode surface or else concentration polarization effects would vitiate the sharpness of the separation from other ions. Rapid stirring also permits higher current densities to be employed with consequent decrease in the time of electrolysis.

In calculating beforehand the limiting cathode potential for an electrolysis, a simple calculation of the equilibrium potential from the Nernst equation is not sufficient. To the equilibrium potential must be added the polarization potential. Since the latter depends on the rate of stirring and on the current as well as on the nature of the metal surface, the limiting potential must be established empirically.

It is of considerable importance that any anodic reoxidation of the metal, if it can exist in more than one valence state, or any reaction between the plated metal and anodic oxidation products be kept at a minimum both to insure the quantitative deposition of the metal at the cathode and to minimize the time required for the deposition. Ways of reducing or eliminating these difficulties include: (1) The use of a reducing agent which will be oxidized in preference to the intermediate valence state, that is, a depolarizer; (2) increasing the initial cathode voltage to a value sufficient to instantly reduce to the metallic state more than half of the intermediate valence state before the latter has been stirred away from the immediate vicinity of the cathode; (3) isolation of the anode by means of a membrane or porous cup; (4) reduction of the anode potential to a value which will not oxidize the intermediate valence state.

INTERNAL ELECTROLYSIS

The term internal electrolysis was applied by Sand[8] to those electrodeposition processes in which an attackable anode is used, and a direct, external wire connection between the cathode and anode is made, so that the electrolysis proceeds spontaneously without the application of an external voltage. The arrangement is really nothing but a short-circuited voltaic cell.

This method is a species of controlled cathode potential electrodeposition, for, if the metal chosen for the anode is the same as the metal in solution from which the separation of another metal is desired, then automatically the cathode potential is decreased as the electrolysis proceeds and the concentration of the metal deposited at the cathode decreases. The limiting potential is simply the electrode potential of the attackable anode metal.

The method is particularly well adapted to the determination of small quantities of one metal in the presence of large amounts of another, for example, the determination of bismuth and copper in lead bullion. If the amount of metal to be deposited exceeds 10 or 15 mg., the deposit is apt to be spongy and some of the metal may diffuse to the anode and be deposited on the anode. No attention is required during the operation, which normally requires 30 minutes.

Although the method has been known for a long time, only recently have applications of it been made in technical analysis. In the apparatus of Sand, the solutions surrounding the anode and cathode are separated by a parchment membrane; in the apparatus of Clarke, Wooten, and Luke,[9] shown in Fig. XV-10, they are separated by an alundum shell, which, when new, must be treated with acids to make it porous. Two anodes are generally used to speed the deposition. The solutions are stirred mechanically, and means are also provided for flushing the anolyte into the catholyte in order to return any metals which may have diffused into the anolyte during the early part of the electrolysis. The electrodes are connected together by a short-circuiting switch. At one time Sargent and Company manufactured a commercial model similar to the one shown in Fig. XV-10.

Obviously, the metal being deposited must be lower in the electromotive series than the metal from which it is being separated, copper and bismuth, in the example cited, being lower than lead. The solution surrounding the anode must have a high electrical conductivity, and this may be secured by a high concentration of electrolyte, usually of acids or ammonium salts. The anolyte must also, however, contain a higher concentration of the ions of the anode metal than does the catholyte; otherwise the anode metal

8. Sand, H. J. S., Analyst, 55, 309 (1930).

9. Clarke, B. L., Wooten, L. A. and Luke, C. L., Ind. Eng. Chem., Anal. Ed., 8, 411 (1936)

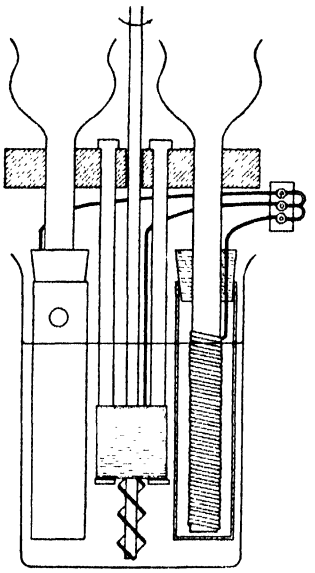

Fig. XV-10. Apparatus of electrodeposition by internal electrolysis

might be deposited at the cathode due to the concentration cell effect. Chloride solutions may be used without the addition of an anodic depolarizer, as the anode reaction is the dissolution of the metal of the anode.

Efforts have been made to eliminate the porous membrane separating the catholyte from the anolyte.[10] Besides being simpler and more convenient to assemble, electrolysis without the membrane permits the separation of metals closer together in the electromotive series, since the internal resistance of the cell is lower. A great disadvantage with this simplified technic, however, is the possibility of depositing the metal on the anode by local cell action on the surface; this can only be circumvented by carefully maintaining the concentration of the metal under a certain limit below which it is not deposited on the anode, and by choosing a metal for the anode which does not give too great a potential difference.

THE MERCURY CATHODE

Electrolysis employing a mercury cathode is a convenient way of removing many metals from

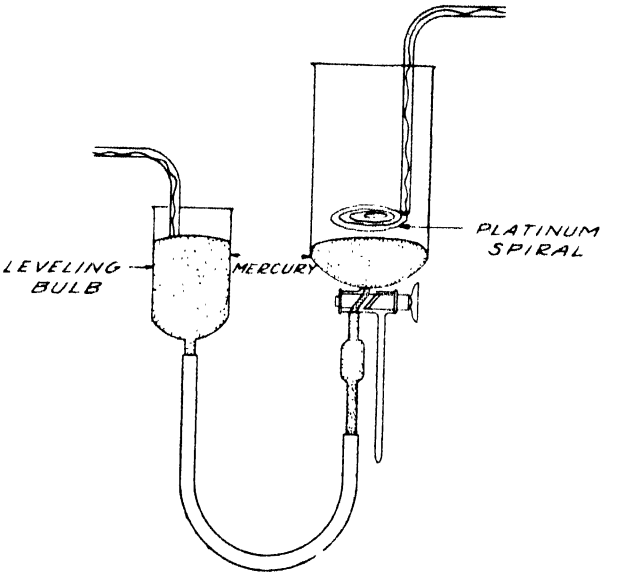

Fig. XV-11. Melaven's mercury cathode cell

solution, although not well adapted to the determination of any of the metals removed, owing to the difficulty of drying and weighing the mercury. The high overvoltage of hydrogen on mercury makes possible the deposition from a fairly acid solution of metals, such as iron, nickel, chromium, and zinc, which could not otherwise be completely deposited from such solutions. If a metal alloys with mercury to form an amalgam, the electrode potential of the alloy is more positive; the metal is also protected to a considerable extent from the solvent action of the acid.

The form of apparatus originally constructed by Melavan[11] for the electrolysis is shown in Fig. XV-11. A platinum wire, usually a spiral, is used as anode; and contact to the mercury is made by a copper wire. A sulfuric acid solution, about 0.1 N in concentration, is generally used as electrolyte. The solution is best stirred mechanically with a stirrer which agitates both the solution and the mercury. When the deposition is complete, the leveling bulb is lowered until the mercury level just reaches the bore of the stopcock. The latter is then turned through 180 degrees and the contents of the electrolyzing vessel rinsed into a beaker for further treatment.

10. Lurie, J. J. and Troitzkaja, M. I., Z. Anal. Chem., 107 34 (1936).

11. Melavan, A. D., Ind. Eng. Chem., Anal. Ed., 2, 180 (1930). See also Evans, B. S., Analyst, 60, 389 (1935).

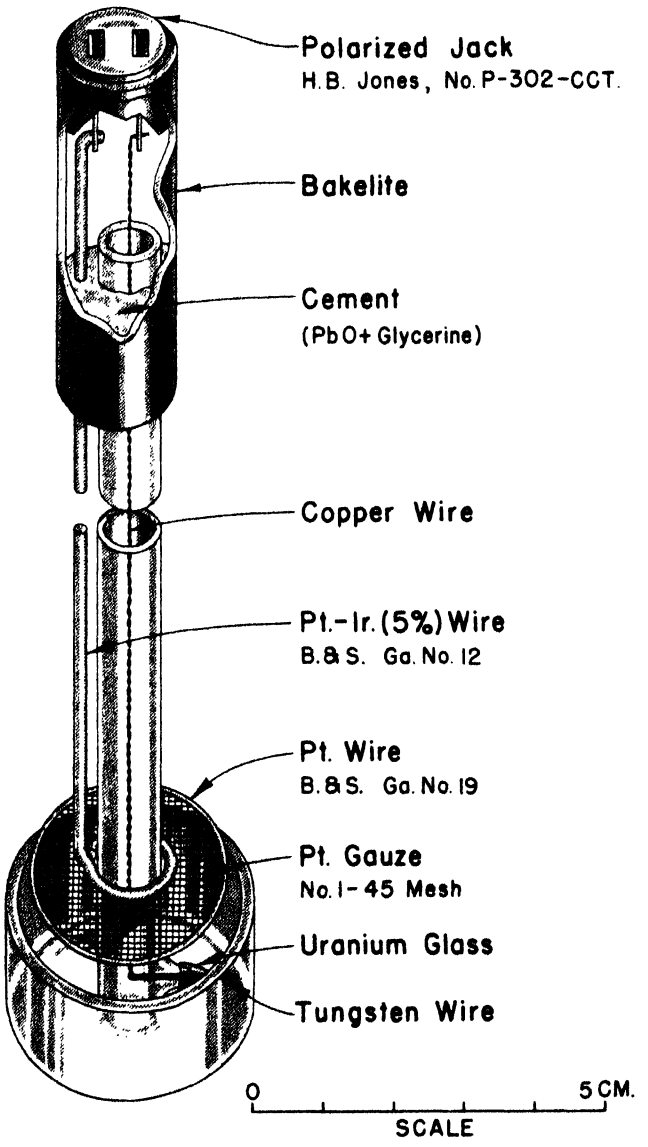

Fig. XV-12. Unitized Mercury Cathode Electrode. (After Johnson, Weaver, and Lykken, Anal. Chem., 19, 481 (1947)

A convenient, unitized apparatus which employs a self-contained immersion electrode assembly has recently been described.[12] Fig. XV-12 shows a diagrammatic sketch of the assembly. Special advantages found in the use of this unitized arrangement include: (1) The electrode is easily washed with a stream of wash liquid, quickly enough so that elements in the amalgam have little opportunity to redissolve; (2) electrolysis with fresh mercury is quickly accomplished simply by interchanging electrode assemblies; (3) less mercury is required, only 10-15 ml. per change, and the difficulty from loss of mercury is minimized.

In general, all the metals below zinc in the electromotive series are deposited on the mercury cathode. The most useful application of the mercury cathode is the removal of heavy metals prior to the determination of such elements as the alkaline earth and alkali groups, titanium, vanadium, tungsten, aluminum, and silicon. Three successive 30-minute electrolysis periods, each with a fresh portion of mercury, suffice to reduce the heavy metal concentration from 0.5 g. to a few hundredths of a milligram.

Lingane[13] has extensively applied electrolysis with a mercury cathode at a carefully controlled potential to remove nobler metals, in devising rapid, systematic schemes of analysis with the polarograph for various alloys. A mercury cathode is uniquely advantageous for controlled electrolytic separations, because the optimum values of the cathode potential may be deduced reliably from the known polarographic characteristics of the metals to be separated.

COULOMETRIC ANALYSIS

By this unique electroanalytical method devised by Lingane,[14] the amount of material which is deposited at a mercury cathode by controlled cathode potential is measured with a hydrogen-oxygen coulometer. The optimum cathode potential is deducible from the polarographic characteristics of the substance concerned, and the quantity of electricity passed is determined with a hydrogen-oxygen coulometer in series with the electrolytic cell. The time required, usually an hour, is practically independent of the concentration of metal ion being determined, but does depend on the geometry of the cell, the area of the mercury cathode, the rate of stirring, and the temperature. A precision of 0.01 milliequivalent for any reducible material is possible. Sharp separation of metals, whose reduction potentials differ by only 0.2 volt, can be performed easily.

12. Johnson, H. O., Weaver, J. R. and Lykken, L., Anal. Chem., 19, 481 (1947). Ibid. with T. D. Parks, 20, 148 (1948).

13. Lingane, J. J., Ind. Eng. Chem., Anal. Ed., 16, 147 (1944). Ibid., 18, 429 (1946).

14. Lingane, J. J., J. Am. Chem. Soc., 67, 1923 (1945).

The coulometric method can be applied advantageously to the determination of the reduction states that correspond to polarographic waves observed in complicated cases where the Ilkovic equation (see Chapter XVI) is inadequate. For example, after complete reduction of a dilute solution of picric acid, the coulometer reading indicated that only 17 electrons per mole of picric acid were involved in the reduction. Complete reduction would have involved 18 electrons. Thus a bimolecular reduction product was postulated for the product.

LABORATORY WORK IN ELECTRODEPOSITION

Electrodeposition with Limited Cathode Potential

General Directions for the Operation of Diehl's Apparatus

Connect the terminal marked GROUND, on the right-hand side of the instrument, to a convenient plumbing pipe making sure that good electrical contact is established, preferably by soldering the connection wire to the pipe.

Turn output voltage selector switch to OFF and plug the line cord from A.C. INPUT into a 110 volt, A.C. line. The blower used to cool the rectifier and voltage regulator is turned on as soon as the line cord is plugged in; air will issue from the opening in the back.

Turn ON the switches marked V.T.V.M. (vacuum-tube voltmeter) filament voltages, amplifier, and DC. output. The center meter (meter of the vacuum-tube voltmeter) will make an initial excursion and settle back to approximately zero; the meter marked plate No. 2 will read some value greater than zero, indicating that the amplifier is working. Allow 5 minutes for the tubes to establish equilibrium, and then calibrate the vacuum-tube voltmeter and the potentiometer. If the calibrations are made immediately they should be checked after a 5 or 10-minute interval.

Voltmeter Calibration. Turn V.T.V.M. input selector switch to OPEN and vary V.T.V.M. zero adjust knob until the meter reads exactly zero. Turn V.T.V.M. input selector switch to D.C. IN and V.T.V.M. range selector switch to 1.0 volt range. Throw V.T.V.M. reversing switch to left. Move amplifier selector switch to STD. CELL. The vacuum-tube voltmeter should read the voltage of the standard cell, 1.0185 volts, indicated by the red line on the scale. If it does not, it can be made to do so by varying the Range Adjust resistance inside the apparatus; this resistance has a slotted shaft extending through the chassis approximately in the center of the apparatus. The voltmeter is now ready to read on any of the four ranges, 0 to 0.5 volt, 0 to 1.0 volt, 0 to 2.5 volts, and 0 to 5.0 volts. If the V.T.V.M. input selector switch is on the D.C. IN position, the voltage measured is that impressed on the D.C. input terminals (in which case the vacuum-tube voltmeter is in parallel with the amplifier). If the V.T.V.M. input selector switch is in the external IN position, the voltage measured is that impressed on the ext. input terminals; this would be the case when the vacuum tube voltmeter is used as a titrimeter.

Check the zero setting of the vacuum-tube voltmeter occasionally during use.

Potentiometer Calibration. Throw the amplifier selector switch to SHORT (center position). Turn the limiting voltage controls, both COARSE and FINE, to zero. Vary the potentiometer zero adjust knob until the relay just closes, as indicated by the pilot light coming on (the Variac will begin to turn at the same time and the milliammeter marked Plate No. 2 will reach a minimum value moving left).

Turn the limiting voltage controls to read the voltage of the standard cell, 1.0185 volts, and throw amplifier selector switch to STD. CELL. Vary the potentiometer adjustment knobs COARSE and FINE until the relay just closes, that is, the pilot light just comes on. This operation adjusts the working current in the potentiometer circuit to such a value that each step on the limiting voltage control coarse dial is exactly 0.1 volt and the full scale of the fine dial is exactly 0.1 volt.

Recheck zero.

Controlled Cathode Potential Electrodeposition. Connect the anode, cathode, and reference cell to the instrument either by (a) individual wires or (b) the shielded four-wire cable. If method (a) is used, connect the anode and cathode to D.C. OUTPUT terminals + and - respectively, and connect the cathode and reference cell to D.C. INPUT terminals, using four wires in all from the cell. Connect the cathode to the negative terminal and the reference cell to the positive. In some cases the cathode may be positive to the reference cell in which case the reversing switch of the vacuum-tube voltmeter will have to be thrown to the right.

If method (b) is used to connect the cell to the instrument plug the four-wire cable into the socket on the right side of the instrument, connect the red wire to the anode, the black and green wires to the cathode, and the white wire to the reference cell. If the cathode happens to be positive to the reference cell, throw the reversing switch of the vacuum-tube voltmeter to the left.

Bring the solution to be electrolyzed up around the electrodes, placing the tip of the reference electrode outside the cathode but as close to it as possible and at about its middle. Start the stirring motor. With the potentiometer and vacuum-tube voltmeter calibrated as described above, the electrolysis may be started. Set the amplifier selector switch on D.C. INPUT and the V.T.V.M. input selector switch on D.C. IN. Set the limiting voltage controls, COARSE and FINE, to the limiting cathode potential desired. Turn the ammeter range Switch to 10,000. (10 amperes full scale), and turn on the D.C. output switch. Adjust the current to a suitable value by turning the voltage selector dial and the variac.

With good stirring a current of 8-10 amperes may safely be used at the beginning of the electrolysis. The size of this current will remain constant for several minutes, depending on the size of the sample taken and on other factors. The cathode-reference cell potential will gradually increase (cathode becoming more negative) as shown by the vacuum-tube voltmeter. When the cathode-reference cell voltage reaches the limiting value set on the controls, the relay will close, as indicated by the pilot light, and the Variac will begin to turn, decreasing the electrolyzing current. This operation is intermittent, the cathode voltage increasing owing to the decrease in the metal ion concentration as the deposition occurs and decreasing each time the control operates to decrease the electrolyzing current owing to the dependence of the catnode overvoltage on the current.

When the current has been reduced to a value less than 1.0 ampere the ammeter range may be changed to the 1000 MAMP. range and again later it may be changed to the 100 MAMP. range.

Discontinue the electrolysis after the current has been reduced to 10 to 30 milliamperes. Remove electrolyte and simultaneously wash the electrodes without interrupting the current.

At the conclusion of the work turn off the vacuum-tube voltmeter, amplifier, and D.C. output. Disconnect the A.C. line cord (necessary in order to turn off blower).

Suggestions for Assembling a Manually Operated Controlled Cathode Apparatus

Equipment. Full wave rectifier capable of furnishing an output voltage of 15 volts and current of 10 amperes; or 2 six-volt storage batteries connected in series, with an adjustable rheostat.

An electronic voltmeter, 0 to 1.0 volt.

A stirrer with rotational speed at least 600 r.p.m.

Three-scale ammeter, 0 to 100, 1000, and 10,000 milliamperes.

Two concentric platinum gauze electrodes. The anode should either be designed for rotating, or else a glass stirrer, which rotates between the two electrodes, should be provided.

Diagram of the Circuit. See Fig. XV-7.

General Instructions.

1. Assemble the apparatus as described in Fig. XV-7. Use double-pole double-throw switches to make connection to the various ammeter ranges. If a Cenco stirrer is used, connection to the rotating anode may be made from any point on the frame of the motor. A Variac, if used to control the input potential to a step-down transformer, in turn providing the input potential to a full-wave selenium rectifier, provides a convenient substitute for the external resistance, R.

2. Insert the platinum electrodes into their respective holders. Start the stirring motor, and adjust the speed to 600-800 r.p.m.

3. Turn on the current and adjust the Variac or adjustable rheostat until a current of 8 to 10 amperes is obtained.

4. When the cathode-reference cell voltage reaches the limiting value, as indicated by the electronic voltmeter, decrease the Variac setting or increase the external resistance sufficiently to maintain the limiting cathode potential.

5. The ammeter connection may be changed to the appropriate range during the course of the electrolysis. Discontinue the electrolysis when the current has been reduced to 10 to 30 milliamperes.

6. Remove electrolyte and simultaneously wash the electrodes without interrupting the current.

Procedure for the Direct Determination of Copper in Bronze. Weigh out accurately into a 300 ml., tall form beaker, 0.5 to 1.0 g. of sample. Add 10 ml. of concentrated hydrochloric and 5 ml. of water. Add, 1 ml. at a time, 5 ml. of 30% hydrogen peroxide (Superoxol). Considerable heat is generated and, if the peroxide is added too rapidly, the action may become too violent; wait until the reaction moderates before adding the next portion. The acid-peroxide mixture will dissolve the sample only if the solution does not become too hot. It may be necessary to cool the mixture during the dissolution process by im-

mersing the beaker in cold water. It can all be added within about 5 to 6 minutes. By this time the sample will have practically all dissolved. Boil gently until the excess of peroxide is decomposed, which will require about 5 minutes, and will be indicated by the absence of small bubbles. By this time the solution of the sample will be complete.

Add 25 ml. of distilled water and 4 g. of hydroxylammonium chloride, or hydrazine hydrochloride. Keep the solution just below the boiling point for 5 or 10 minutes, until the dark green color which first appears becomes much lighter, indicating considerable reduction to the chlorocuprous complex ion. Add 5 ml. of concentrated hydrochloric acid. Dilute the solution sufficiently to cover the electrodes and proceed with the electrolysis.

An alternative method of dissolving the sample is to add 10 ml. of concentrated hydrochloric acid, heat, and cause the sample to dissolve by the dropwise addition of nitric acid. Avoid adding an excess of nitric acid. When the sample has dissolved, wash the cover glass and beaker, add 20 ml. of concentrated hydrochloric acid and 4 g. of hydroxylammonium chloride. Keep the solution just below the boiling point until the green color is much lighter.

Electrolyze with vigorous stirring using a limiting cathode potential of -0.35 volt against a saturated calomel reference electrode. The current should have an initial value of at least 8 amperes so that the initial cathode potential quickly reaches a value of at least -0.30 volt. Copper may not deposit for several minutes after the electrolysis is started and the saturated calomel cell may be negative to the cathode at the start. Copper will begin to plate when the cathode becomes about 0.2 volt negative to the saturated calomel cell. Wash down the walls of the beaker once or twice during the electrolysis. Continue the electrolysis until the current has been decreased to about 0.03 ampere.

Complete the detemination in the usual manner, removing the electrolyte before turning off the current. Wash the deposit of copper with water and then with alcohol and dry at a temperature not exceeding 100° C. for 10 minutes.

Notes:

1. If less than half of the copper is initially reduced to the chloro-cuprous complex ion by the hydroxylammonium chloride, or if too low an initial current density is used, the copper may partially plate and then slowly redissolve. When this is observed, discontinue the electrolysis, add 0.5 ml. of 50% stannous chloride solution, and begin the electrolysis by increasing the variac or voltage output control.

2. No calomel should be present in the salt bridge as it will slowly diffuse into the electrolysis cell. Its presence will be detected by the electrolytic solution assuming a yellow or orange coloration. If this occurs, the sample must be discarded. Low results always are obtained.

3. If the cathode-calomel voltage, or limiting cathode potential, is allowed to exceed 0.40 volt, tin will deposit as a black film and the result will be high.

4. When the current has decreased to a small value, it may be necessary to reduce the speed of stirring, in order to allow the current to decrease to from 10 to 30 milliamperes.

Methods for the Separation of Other Metals

The literature dealing with the subject of electrodeposition with limited cathode potential is not very extensive. In fact, only recently has the subject received any serious attention. Therefore, methods for the separation of some of the metals, including references to the literature, follow:

Bismuth. Best deposited from a hot sulfuric acid,[15] or a hot nitric acid solution containing oxalic acid.[16] Satisfactory results are also obtained from alkaline tartrate solutions - a separation from copper.[17] Cathodic depolarizers must be present.

Cadmium. Deposited from an acetic acid[18] or an alkaline cyanide solution.[19]

Nickel. Deposited from a warm ammoniacal solution.[20] All the sulfide group metals must be removed prior to the separation of the nickel.

Silver. Deposited from a 10% ammoniacal solution containing hydrogen peroxide.[21] Lead and nickel interfere.

15. Kny-Jones, F. G., Analyst, 64, 575 (1939).

16. Ibid., 172 (1939). Also Collin, E. M., ibid., 54, 654 (1929).

17. Kny-Jones, F. G., Analyst, 66, 101 (1941).

18. Sand, H. J. S., J. Chem. Soc., 91, 401 (1907).

19. Crouthamel, Brouns, and Diehl, unpublished work but partly included in H. Diehl, "Electrochemical Analysis with Graded Cathode Potential Control," G. F. Smith Chemical Co., Columbus, 1948, p. 52.

20. Torrance, S., Analyst, 63, 488 (1938).

21. Miller, W. L., Ind. Eng. Chem., Anal. Ed., 8, 431 (1936).

Tin. Deposited from a chloride solution. Special precautions are necessary including the presence of a depolarizer.[22]

A general discussion of depolarizers has been treated by Lindsey and Sand.[23]

INTERNAL ELECTROLYSIS SEPARATIONS

General Instruction for the Operation of Sargent Apparatus

The Sargent internal electrolysis apparatus consists of an electrode holder for the two anodes and cathode, a motor stirrer, a reservoir for the anolyte solution, and a small hot plate to maintain the electrolytic solutions at the proper temperature during deposition.

1. Slip the two anodes over the short length of 3 mm. glass tubing connected to the reservoir, and into the clip holders. The anodes are 20 cm. lengths of coiled wire of the particular attackable anode metal. Cover each anode with a porous alundum shell, which, when new, must be treated with a nitric-tartaric acid mixture to make them conducting.
2. Clamp the platinum gauze cathode into its holder. Likewise insert the glass stirring rod into its chuck. The stirrer is shaped to push the catholyte liquid toward the cathode.
3. Fill the anode compartments with the anolyte solution. Partially immerse the electrodes with the sample.
4. Connect the power plug to a 110 volt, 60 cycle main.
5. Start the stirring motor and close the short-circulating switch.

Determination of Bismuth and Copper in Lead Alloys

One of the most useful applications of the method is the separation of copper and bismuth from lead.[24] A lead anode surrounded by a solution containing 3% nitric acid and 5% lead nitrate is used. The copper and bismuth are plated together on a platinum cathode from a dilute nitric acid solution and at a temperature of 65° to 90° C. The copper plus bismuth plate may be weighed, and one or both metals subsequently determined by the usual methods.

22. Kny-Jones, F. G., Lindsey, A. J. and Penney, Analyst,,65, 498 (1940).

23. Lindsey, A. J. and Sand, H. J. S., ibid., 60, 739 (1935).

24. Clarke, B. L. and Wooten, L. A., Trans. Am. Electrochem. Soc., 76, 63 (1939).

Procedure. Dissolve 10 g. of the sample in a mixture of 1 g. of tartaric acid and 80 ml. of nitric acid in a 400 ml. beaker. Heat gently until solution is complete. Boil for 1 minute to expel the nitrous oxide fumes. Dilute to 150 ml. with distilled water and cool to 40° C. Add 1% potassium permanganate solution while stirring until the solution acquires a violet tint which persists for over a minute.

Dilute the solution until the electrodes are partially covered. Adjust the temperature to 70° C. Add 0.3 g. of urea and electrolyze with stirring using a lead-platinum couple. Once or twice during the electrolysis, flush out the anode chambers, wash down the sides of the beaker and anode chambers, and add small amounts of urea.

When the plating is completed in 20 to 30 minutes, as indicated by failure to plate on a fresh surface when the solution level is raised, quickly remove the electrolyte and wash the platinum electrode with distilled water.

REMOVAL OF METALS AT THE MERCURY CATHODE

Electrolysis at the mercury cathode is a convenient, clean separation of certain metals prior to the determination of those elements which are not deposited. Several factors must be taken into consideration if optimum operating conditions are to be selected: (1) The amount of metal remaining in solution after electrolysis is approximately inversely proportional to the current used and to the area of the mercury surface. A current of 5 amperes is recommended. (2) The optimum distance between anode and cathode surfaces is between 8 and 10 mm. (3) Agitation of the mercury surface, or frequent replacement of the mercury, aids the deposition. If the unitized apparatus of Johnson, Weaver, and Lykken is used, the recommended cell surface area is 10 sq. cm., when used for removing 0.5 g. of material. Three or four changes of mercury at intervals of 15 to 30 minutes are advisable.

A suggested experiment with the mercury cathode involves the separation of 0.5 g. samples of iron, copper, or nickel from a sulfuric acid solution. The amount of the heavy metal remaining after each step of the electrolysis can be determined colorimetrically using the indicated reagents: Copper by diethyldithiocarbamate,[25]

25. Sandell, E. B. "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, 1944, p. 221.

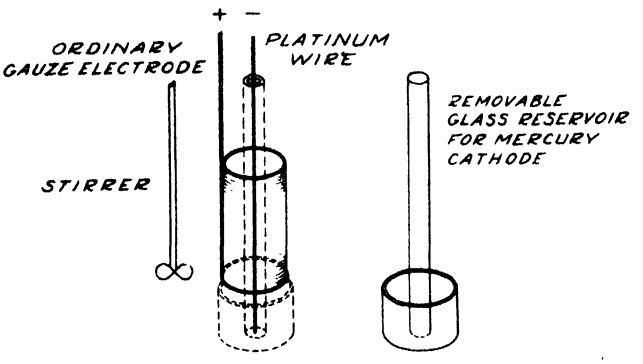

Fig. XV-13. Author's mercury cathode cell assembled from easily obtainable materials

iron by ortho-phenanthroline,[26] and nickel by dimethylglyoxime.[27]

Apparatus. One or more unitized, self-contained cells as shown in Fig. XV-12, or the substitute found satisfactory by the authors, shown in Fig. XV-13.

6-Volt source of direct current up to 5 amperes, from either a tungar rectifier or other type rectifier.

Procedure. Concentrate the neutral or slightly acid solution to be electrolyzed to 25 or 30 ml. and transfer it to a 300 ml., tall form beaker.

26. See p. 23 of chapter II.
27. See p. 24 of chapter II.

Fill the cathode compartment with fresh mercury to within 1 to 2 mm. of the top, and raise the electrolytic beaker around the cathode until the electrode almost touches the bottom of the beaker. The equivalent of 1 ml. of concentrated sulfuric acid should be present in the solution. Turn on the current and adjust the resistance until a current of 5 amperes is attained. Cover the beaker with a split notched watch glass and electrolyze for 15 to 30 minutes. Add water as necessary to maintain constant volume. An auxiliary motor stirrer rotating slowly at the level of the mercury cathode surface materially speeds the rate of deposition by bringing fresh ions to the cathode surface.

After the first electrolysis period, with the current on, lower the beaker and immediately rinse the electrode with a stream of distilled water. Replace the amalgam with clean mercury, electrolyze for 15 to 30 minutes, and rinse; repeat this cycle one or more times until the removal of the heavy metal is considered complete.

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1. Diehl, H., "Electrochemical Analysis with Graded Cathode Potential Control," G. F. Smith Chemical Co., Columbus, 1948.
2. Fischer, A., and Schleicher, A., "Electroanalytische Snellmethoden," 2nd. Edition, F. Enke, Stuttgart, 1926.
3. Sand, H. J. S., "Gravimetric Electrolytic Analysis," Vol. II, Blackie and Sons, London, 1940.

CHAPTER XVI

POLAROGRAPHY

THEORETICAL PRINCIPLES

Introduction. Reconsider for a moment the electrical circuit that was employed for electrodeposition by means of graded cathode potential. The potential of the cathode was measured during the course of the deposition through the use of an auxiliary circuit consisting of a calomel reference cell in conjunction with the cathode. However, if the size of the electrode under observation were decreased sufficiently, and the area of the other electrode surface were made relatively large, the use of an auxiliary reference electrode could be eliminated and the potential difference between the anode and cathode measured directly. The polarization of the large electrode will be practically constant due to the smallness of the current which would be flowing, thus it is able to function as a reference electrode since its potential remains almost constant. Hence variations in the e.m.f. of the cell will be due almost entirely to changes in the potential of the microelectrode since only a minute potential difference is needed to overcome the ohmic resistance of the electrolyte. Consequently the microelectrode can function as an indicator electrode to measure changes in potential while current is flowing.

Heyrovsky and Kuceras[1] devised such a technique and Heyrovsky and Shikata[2] developed the polarograph to register automatically the changes in current observed when the e.m.f. applied between the two electrodes is varied. The simplicity of the electrical circuit and the availability of the equipment required is apparent from Fig. XVI-1. It consists of an accurate slide wire through which a steady current passes. The potential drop across the slide wire is adjusted to any desired value, which is read on the voltmeter, V, by inserting one, two, or three dry cells in series and regulating the voltage by means of a series resistance, R. The slide wire contact is

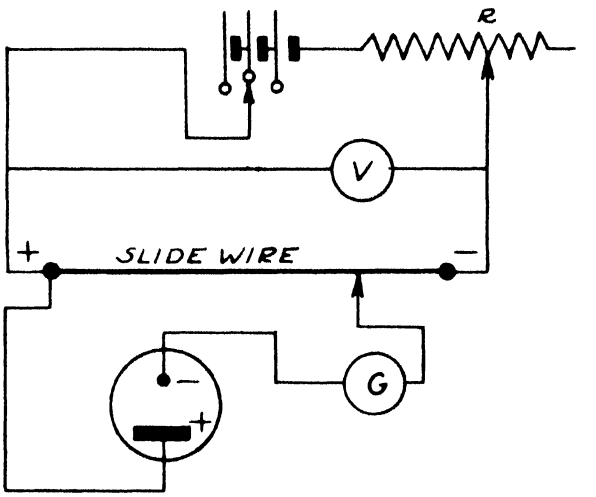

Fig. XVI-1. Basic circuit of polarography

moved to vary the e.m.f. applied to the two electrodes. At each voltage setting the current passing through the electrolytic cell is measured by a suitable galvanometer, G, in series.

Limiting Current Curves

The phenomenon of the limiting current obtained with the use of microelectrodes is caused by the extreme state of concentration polarization which results from the depletion of the electroactive material in the immediate vicinity of the electrode surface as a result of the electrode reaction. For example, consider an electrolytic cell containing a large nonpolarizable mercury pool serving as anode and a small platinum wire microelectrode dipping into a dilute solution of cadmium chloride. The individual potential of the microelectrode is indeterminate and variable and will assume any potential applied to it from an external source. Such an electrode is said to be polarized whenever it acquires a potential different from that which it has in the absence of electrical connections.

Now let us consider what will happen if an external e.m.f. is applied to the cell in such a direction that the microelectrode is made negative with respect to the reference anode. All the positively charged ions present in the solution will be attracted toward the microelectrode by two forces: (1) A diffusive force, due to the concentration gradient produced at the electrode surface; and (2) an electrical force, due to the attraction of oppositely charged bodies to each other. Electroactive ions are therefore supplied to the microelectrode surface partly through diffusion and partly by electrical migration. The

1. Heyrovsky, J., Chem. Listy, 16, 256 (1922).
2. Heyrovsky, J. and Shikata, M., Rec. trav. chim., 44, 496 (1925).

total current passing through the electrolytic cell can be regarded as the sum of these two factors.

A typical current-voltage curve is shown in Fig. XVI-2. From A to B practically no current will be observed to flow. The potential of the microelectrode, being perfectly polarizable, adopts the correspondingly increasing negative potential applied to it. However, when point B is reached, the current suddenly begins to increase. The potential of the microelectrode has been made equal to the decomposition potential of the cadmium ions with respect to a metallic cadmium electrode. Consequently the microelectrode be-

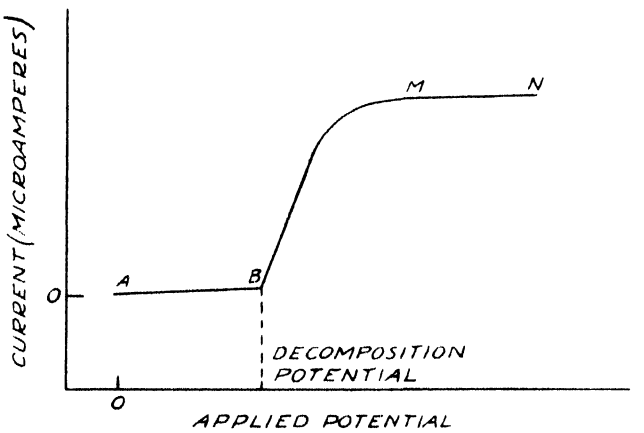

Fig. XVI-2. Typical current-voltage curve

comes depolarized by the cadmium ions which are then discharged upon the electrode surface to form metallic cadmium. As a result of the electrode process taking place, a rapid increase in current flowing through the electrolytic cell will be noted.

Up to this point a similar sequence of events is observed during electrolytic processes employing large electrode surfaces. However, the analogy ends when point M is reached on the curve in Fig. XVI-2, for it is noticed that the current no longer increases linearly. Instead, as the potential applied to the microelectrode is continually made more negative, the current approaches a steady limiting value at point N and no increase is noted at higher cathodic potentials unless a second substance able to depolarize the microelectrode is present in the solution. At any point between B and M in Fig. XVI-2, the number of cadmium ions reaching the electrode surface as a result of diffusion and migration from the main body of the solution always exceeded the number of cadmium ions which reacted at the electrode and deposited upon the surface of the electrode. At point M the rate of supply of the cadmium ions from the bulk of the solution to the electrode surface has become equal to the rate of their deposition. Therefore, at potentials more negative than point N, the concentration of undischarged cadmium ions at the electrode surface is negligibly small in comparison with the cadmium-ion concentration in the bulk of the solution. No further increase in current passing through the electrolytic cell can be expected, since the limiting current is now fixed by the rate at which the cadmium ions are able to reach the electrode surface.

Indicator Electrodes.

Stationary solid microelectrodes of various forms and constructed from various metals have been used in determining current-voltage curves. Usually noble metals are employed, but any metal is suitable as long as its ions exist in the solution in such small concentration that they do not influence the ratio of the oxidant and reductant present; that is, the metal is more electropositive than the region of voltages under investigation. In practice this type of microelectrode has certain disadvantages. The current does not become constant upon applying a given potential until after a wait of several minutes, and even then the current slowly decreases with time. The overvoltage of hydrogen on platinum and on most metals which can be plated on the electrode is small, so that the evolution of hydrogen interferes with many reductions which might otherwise be carried out. Also the temperature coefficients of the observed diffusion currents are higher than with any other type of indicator electrode, about 4% per degree. However, stationary noble metal microelectrodes do have one definite advantage, in that their only limitation in the direction of positive potentials is the evolution of oxygen, assuming other electro-oxidizable materials are absent; whereas, with less noble metals, anodic dissolution of the electrode metal occurs at relatively small positive potentials. Currents obtained are reproducible.

A microelectrode rotating at constant speed eliminates the disadvantage of waiting for a steady current and the temperature coefficient of the limiting current is only about 2%, but the limiting current is not reproducible.

The best form of a solid microelectrode consists of a platinum wire about 3 mm. long and 0.5 mm. in diameter, sealed into a piece of glass tubing into which mercury is introduced for electrical contact. If the microelectrode is to be rotated, the tubing is mounted in the chuck of a motor rotating at a constant speed of about

600 r.p.m. Kolthoff and Lingane,[3] and Laitinen[4] have described various forms and their characteristics.

The most satisfactory indicator microelectrode for studying current-voltage curves is a slowly growing drop of mercury issuing from a glass capillary, about 0.05 mm. in diameter and 6 cm. in length, in small uniform drops. This type of electrode has the following advantages, as pointed out by Müller,[5] which cannot be matched by any other indicator electrode: (1) Its surface is reproducible, smooth, and continually renewed; (2) the surface area can be calculated; (3) mercury amalgamates with most metals; (4) the value of the overvoltage of hydrogen is highest on mercury so that much work can be done in acid solutions and at large negative potentials without interference from the evolution of hydrogen; and (5) the current assumes a steady value immediately and is reproducible.

Reference Electrodes.

In the early work with dropping mercury electrodes, a mercury pool covering the bottom of the electrolysis cell served as the nonpolarizable reference electrode. If the solution covering the pool contains chloride or other depolarizing ions, the mercury pool simply acts as a calomel or other type of reference electrode of that approximate concentration. While convenient, the mercury pool suffers from the disadvantage of not possessing a definite, known potential. Consequently, its potential must be determined after each current-voltage curve has been obtained by balancing against some standard half-cell. Particularly in nonaqueous solutions, the pool potential may vary widely.

Kolthoff and Lingane introduced the use of an external standard reference electrode connected to the electrolytic vessel by means of some type of salt bridge. If the area of the external electrode is relatively large, the small currents passing through the cell will not appreciably alter its potential. Thus all of the potential values are immediately referred to a standard electrode, and the uncertainty of the pool correction need not be considered. The saturated calomel electrode is perhaps the most convenient to use, although silver-silver chloride half-cells have also been used successfully. In some instances a wire of some metal has simply been wrapped around the dropping mercury capillary to serve as reference. Knowing the potential of the nonpolarizable reference electrode, E_R, we can calculate the potential of the polarized microelectrode, E_m, from the applied voltage, V, and the observed current, I, by means of Ohm's law:

$$E = E_R + E_m + IR \qquad (1)$$

where R is the resistance of the electric circuit. The correction for IR becomes necessary whenever the product of the current and resistance exceeds 1 mv. Most current-voltage curves must be corrected before they become current-potential curves.

Factors Affecting the Limiting Current

Residual Current. Various factors are known to influence the limiting current. If a current-voltage curve is determined for a solution containing no apparent electrolyzable material, it is observed that a small current will flow over the entire potential range. With the dropping mercury electrode this small current partially arises from the fact that as each drop of mercury grows, a small current must flow in order to build up the charge on the mercury corresponding to the applied potential. With stationary or rotating microelectrodes, the charging current is zero because the electrode area is constant with time, but, nevertheless, a small current due to unknown causes still flows. Obviously this residual current must be subtracted from the total current observed during the reaction of some electroactive material in order that the actual current flowing due to the reaction may be known. In practical work this residual current is automatically subtracted by proper extrapolation and placement of tangents to the wave.

Migration Current. Previously it was mentioned that electroactive material normally is able to reach the electrode surface by two major processes. One is the migration of charged particles in an electric field caused by the potential difference existing between the electrode surface and the solution. The other is diffusion of particles toward the electrode due to the concentration gradient produced in an area of about 0.05 mm. radius about the electrode caused by the removal of material at the electrode surface as a consequence of an exchange of electrons.

It will be recalled from electrochemical work that the current is carried through an electrolytic

3. Kolthoff, I. M. and Lingane, J. J., "Polarography," Interscience Publishers, Inc., New York (1941), pp. 439-41.

4. Kolthoff, I. M. and Laitinen, H. A., J. Am. Chem. Soc., 61, 3344 (1939).

5. Müller, O. H., "The Polarographic Method of Analysis," Mack Printing Co., Easton, Pa., 1941. p. 24.

solution impartially by all the ions present, regardless of whether or not the ions take part in any electrode reaction when they reach the electrode surface. The fraction of the total current carried by each ion species will depend upon its transference number in the particular solution in question.

For example, let us suppose an electrolytic solution is composed of potassium ions, 0.10 M, and cadmium ions, 0.01 M. If the equivalent conductances of each ion are approximately equal, it is evident that approximately 90% of the current will be transported to the negative electrode by the potassium ions, and only 10% by the cadmium ions. Both will have a definite tendency to diffuse toward any portion of the solution where a concentration gradient exists, but the rate of diffusion will be slow. Now if the concentration of potassium ions be increased until they represent 99% of the total cations present, practically the entire current passing through the electrolytic cell will be transported by the potassium ions. Consequently, as Heyrovsky[6] originally pointed out, the migration current of the electroactive material can be practically eliminated if there is added to the solution an indifferent or supporting electrolyte in a concentration that is at least 100-fold that of the electroactive material. Under these conditions the electroactive material can reach the electrode surface only by diffusion, since practically all of the current will be carried by the ions of the indifferent or supporting electrolyte. Often these supporting electrolytes will consist of buffer mixtures for maintaining a constant pH. However, the supporting electrolyte must be composed of ions which are discharged at potentials which will not interfere nor interact chemically with the ions under investigation.

Of course, it must be remembered that after a short interval of electrolysis, the concentration of indifferent electrolyte around the immediate vicinity of the microelectrode will exceed its concentration in the bulk of the solution. A diffusion gradient is then set up whereby these ions are returned to the main body of the solution. Thus a cycle is soon set up for the supporting electrolyte; migration to the electrode, and diffusion back to the bulk of the solution. The actual current carried through the solution, by whatever means, is only equal to the amount of electroactive ions which diffuses to the electrode surface and takes part in the electron exchange.

6. Heyrovsky, J., Arhiv. Hem. i Farm., 8, 11 (1934).

Diffusion Current. On the basis of diffusion theory, Ilkovic[7] derived the following equation for the diffusion current at the dropping mercury electrode:

$$i_d = k\,n\,F\,C\,D^{\frac{1}{2}}m^{2/3}t^{1/6} \quad \text{Temperature constant and no stirring} \quad (2)$$

in which the constant k arises from the geometric characteristics of the dropping electrode; nF is the number of coulombs involved per mole of electrode reaction; C is the millimolar concentration per liter of electroactive material; D is the diffusion coefficient of the electroactive material in $cm.^2/sec.$; m is the mass of mercury flowing through the capillary in milligrams per second; and t is the drop time in seconds at the half-wave potential. The measured diffusion current of various substances has been found to be in good agreement with that calculated from the Ilkovic equation.[8] Thus it can be seen that diffusion currents are governed by several factors - those concerned with the diffusion process itself, such as temperature, viscosity, ion mobilities and ionic strength of the solution; and those dealing with the characteristics of the capillary and of the electrode surface at which the diffusing material reacts.

The last two quantities in the Ilkovic equation, $m^{2/3}t^{1/6}$, are important because they establish a relationship by means of which diffusion currents measured with different capillaries, and with the same capillary at different potentials, may be compared. To make such a comparison, it is necessary only to determine the mass of mercury flowing per second through each capillary at any potential and with any solution, and the drop time at the diffusion current region. The drop time will vary as the applied potential changes due to the change in the surface tension of mercury with applied potential. In fact the drop time closely follows the electrocapillary curve for mercury, Fig. XVI-3, being maximal at the electrocapillary zero, -0.52 volt vs. S.C.E., and decreasing gradually on either the negative or positive side of the electrocapillary zero.

The influence of temperature on the diffusion current is quite marked because the equivalent conductance of most ions changes about 2.5% per degree and the viscosity of mercury is also affected. Actually the diffusion currents of most

7. Ilkovic, D., Coll.Czeck. Chem. Commun., 6, 498 (1934). See also a more exact derivation: MacGillavry, D. and Rideal, E. K., Rec. trav. chim., 56, 1013 (1937).

8. Lingane, J. J. and Kolthoff, I. M., J. Am. Chem. Soc., 61, 825 (1939).

metal ions increase about 2% per degree rise in temperature, which implies that the temperature of the water bath must be controlled to at least $\pm$ 0.5° C.

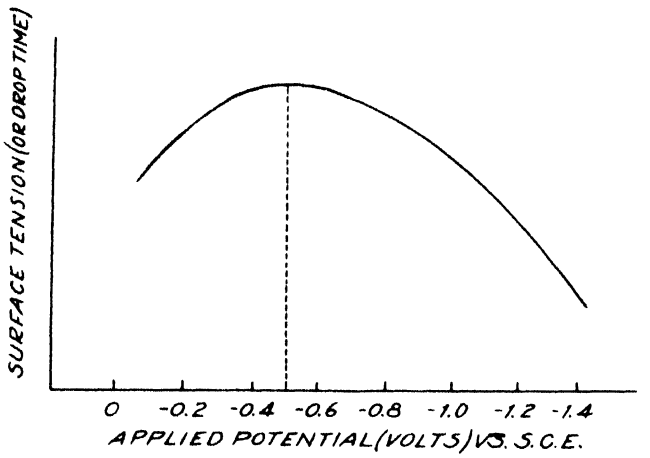

Fig. XVI-3. Electrocapillary curve for mercury

Unless the individual mercury drops fall under their own weight when they are completely formed, no reproducible diffusion currents can be obtained and the method becomes useless. Therefore, no stirring effects can be tolerated.

In contrast to the dropping mercury electrode, when a steady state of diffusion is attained at solid microelectrodes, the actual diffusion current is given by the following expression which is derived from Fick's first law of diffusion:

$$i_d = \frac{AD}{l} nFC = knDC \qquad (3)$$

where C is the concentration of the electroactive material with a diffusion coefficient, D, diffusing through a diffusion layer of effective thickness, l, to an electrode of area A. n is the number of electrons involved in the electrode reaction, and F is the faraday.

The influence of temperature on the diffusion current is more marked with the stationary microelectrodes and, therefore, the temperature of the solution must be controlled within $\pm$0.25°C. Moreover, it has been found that the diffusion current of some ions was markedly altered with changing electrolyte content of the solution.

Oftentimes when rotating microelectrodes are employed, the observed diffusion current is disappointingly small as compared with a stationary microelectrode. It has been pointed out that the appearance of a limiting current region on a current-voltage curve requires the electrode reaction to be rapid in comparison with the rate of diffusion. With a rotating electrode the current density is increased tremendously for a given solution, as compared with a stationary electrode, and it is therefore necessary to determine for each particular case whether current-voltage curves with well-defined diffusion or limiting current regions can be obtained.

Adsorption Currents. Current-voltage curves obtained with the dropping mercury electrode are frequently distorted by maxima unless measures are taken to prevent their occurrence. These maxima vary in shape from sharp peaks to rounded humps, which gradually decrease to the normal diffusion current plateau as the applied voltage is increased (Fig. XVI-4). Their

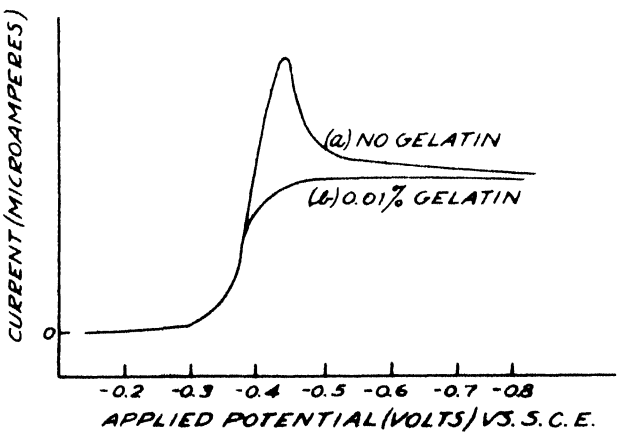

Fig. XVI-4. Maximum obtained with lead ion. (a) No gelatin present; (b) 0.01% gelatin added

presence may indicate that, during part of the current-voltage curve, there is a concentration of the electroactive substance in the diffusion layer which is in excess of that in the main body of the solution. A rigid explanation is lacking, although some investigators believe the stirring effect of the growing drop to be responsible; others believe it due to adsorption of electroactive material on the electrode surface. Maxima are especially prevalent when the decomposition potential is considerably removed from the electrocapillary zero of mercury.

Whatever the cause, maxima must be eliminated in order to measure the true diffusion current. Fortunately, maxima can be easily suppressed by surface active agents such as dye ions or colloids. Gelatin is most often used now, but the amount present in the solution must be carefully controlled between 0.002 to 0.01 %.[9] Less is useless, more will suppress the true dif-

fusion current. Generally the proper amount of gelatin is added to every solution prior to determining the current-voltage curve, whether thought necessary or not, as a precautionary measure.

Half-Wave Potentials and Their Significance

A typical current-voltage curve, or polarogram, is reproduced in Fig. XVI-5. If this polarogram is compared with a typical potentiometric titra-

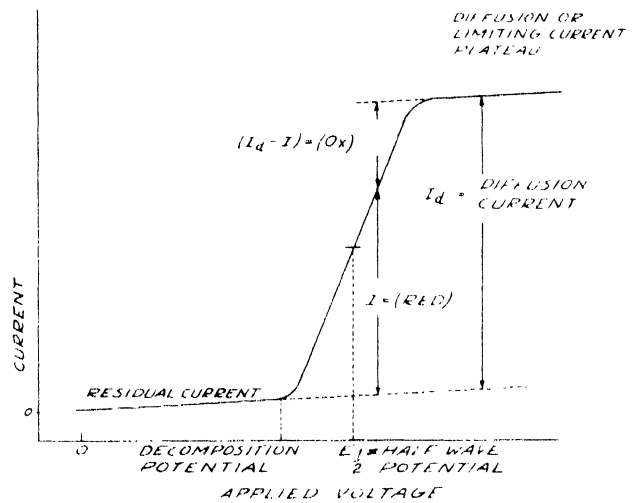

Fig. XVI-5. Typical cathodic polarogram

tion curve, it will be noted that the two are similar. The midpoint of both curves represents the characteristic potential of the particular oxidation-reduction system they illustrate. Yet the conditions under which these curves are obtained are quite different. In the polarographic method only the ratio of oxidant to reductant present at the microelectrode interface is altered by means of the electric current; whereas in the potentiometric method the ratio is changed throughout the entire solution by adding a titrating agent.

In order to derive the equation of a polarographic wave, let us consider a generalized oxidation-reduction reaction which is reversible in a thermodynamic sense:[10,11,12]

$$Ox + n\,e \rightarrow Red \qquad (4)$$

Here Red represents the same substance as Ox but differs by n in the number of negative charges e; together they form an oxidation-reduction system. For reversible reactions, the potential at any point on the wave is given approximately by the familiar Nernst equation at 25°C:

$$E = E^{o} + 0.0591/n \log \frac{a_{ox}}{a_{red}} \qquad (5)$$

where a_{red} and a_{ox} are the activities of the reductant and oxidant, respectively, as they exist at the electrode interface and not those existing in the body of the solution. Since the precision of the polarographic method is not very great, for convenience, the less accurate form of the above equation using actual concentrations instead of activities will be employed:

$$E = E^{o} + 0.0591/n \log \frac{[Ox]_i}{[Red]_i} \qquad (6)$$

The subscripts i denote that we are dealing with concentrations at the electrode/solution interface only.

Before the commencement of the polarographic wave only a small residual current flows. Thus the concentration of any electroactive material must be the same throughout the solution as at the electrode interface. As soon as the decomposition potential is exceeded, some of the material undergoes an electron exchange at the interface; and, as the concentration of the electroactive ions at the interface decreases, the rate of diffusion of these ions from the main body of the solution to the interface increases. The current that flows then is dependent upon the diffusion rate, which in turn is a function of the concentration gradient that results between the depleted interface and the bulk of the solution. In the case of cathodic waves it may be expressed as follows:

$$i = K([Ox] - [Ox]_i)\, D_{ox}^{1/2} \qquad (7)$$

where $K = k\,n\,F\,m^{2/3}t^{1/6}$, terms from the Ilkovic equation: i is the current at any instant on the polarographic wave after suitable correction has been made for the residual current; [Ox], the concentration of oxidant in the main body of the solution; and $[Ox]_i$, the concentration of the oxidant at the electrode interface.

Ultimately, the concentration of oxidant at the interface falls to zero as the applied e.m.f. is increased, and the diffusion current then depends

9. Buckley, F. and Taylor, J. K., J. Res. Natl. Bur. Stds, 34, 97 (1945).

10. Heyrovsky, J. and Ilkovic, D., Coll. Czech. Chem. Commun., 7, 198 (1935).

11. Lingane, J. J., J. Am. Chem. Soc., 61, 2099 (1939).

12. Muller, O. H., "The Polarographic Method of Analysis," Mack Printing Co., Easton, Pa., 1941.

only on the concentration of the reducible substance in the main body of the solution:

$$i_d = K\,[Ox]\,D_{ox}^{1/2} \tag{8}$$

$$\text{Therefore,}\quad [Ox]_i = \frac{(i_d - i)\,D_{ox}^{1/2}}{K} \tag{9}$$

In the case of metals that form amalgams with the dropping mercury electrode, the concentration of the amalgam formed at any point on the wave is directly proportional to the current,

$$i = K[Hg(Red)]_i\,D_{Red}^{1/2} \tag{10}$$

where K has the same value as before. Therefore,

$$[Hg(Red)]_i = \frac{i}{K\,D_{red}^{1/2}} \tag{11}$$

Now substituting these values for the concentrations of reductant and oxidant at the electrode interface into our original equation (6):

$$E = E^o + \frac{0.0591}{n}\log\frac{i_d - i}{i} + \frac{0.0591}{n}\log\frac{D_{red}^{1/2}}{D_{ox}^{1/2}} \tag{12}$$

$$= E^o + \frac{0.0591}{n}\log\frac{i_d - i}{i} + K' \tag{13}$$

The half-wave potential, designated by $E_{1/2}$, is defined as the potential of the microelectrode at the midpoint of the polarographic wave - that is, when one half of all the oxidant which reaches the electrode during a finite time is reduced to the corresponding reductant. Therefore, the concentrations of oxidant and reductant at the interface may be taken as equal if their diffusion rates are identical, a condition approximated in most reversible polarographic reactions. Then at the half-wave potential, i is equal to $(i_d - i)$ by our definition, so that the logarithmic term drops out and equation (13) becomes simply

$$E_{1/2} = E^o - K' \tag{14}$$

Thus the polarographic half-wave potential is closely related to the potentiometric electroactivity value. Usually K' is small and can be neglected since it involves the ratio of approximately equal diffusion coefficients. Substituting the value of the half-wave potential found by equation (14) into equation (6), we obtain the equation for the potential as a function of the current at any point on the polarographic wave:

$$E = E_{1/2} + \frac{0.0591}{n}\log\frac{(i_d - i)}{i} \tag{15}$$

Occasionally with dropping mercury electrodes when the reduction to the metallic state does not result in the formation of amalgams, and always with solid microelectrodes, the concentration or activity of the solid state formed is constant. Hence the equation of the wave will be

$$E = E^o + \frac{0.0591}{n}\log[Ox]_i \tag{16}$$

$$= E^o + \frac{0.0591}{n}\log\frac{(i_d - i)D_{ox}^{1/2}}{K} \tag{17}$$

and the half-wave potential will be given by

$$E_{1/2} = E^o + \frac{0.0591}{n}\log\frac{i_d}{2} + \frac{0.0591}{n}\log\frac{D_{ox}^{1/2}}{K} \tag{18}$$

$$= E^o + \frac{0.0591}{n}\log\frac{[Ox]}{2} \tag{19}$$

The reduction from one oxidation state to another follows equation (12), and the half-wave potential is given by equation (14).

The treatment for anodic waves would be similar. Thus, being independent of the concentration of electroactive material in many instances and of electrode characteristics, half-wave potentials can sometimes serve for the qualitative identification of an unknown material. In practice this is seldom done, since the close proximity of the many different possible half-wave potentials precludes any identification unless the number of possibilities is strictly limited by the character of the unknown.

According to equation (15), a graph with the value of log $(i_d - i)/i$, where i is the current at any point on the polarographic wave (minus the residual current), plotted against the corresponding potential of the microelectrode should be a straight line having a slope of n/0.0591 for a reversible reaction. Consequently, n, the number of electrons taking part in the reaction, may be determined. The intercept of the plot with the zero log current line gives the half-wave

potential of the system, Fig. XVI-6. Any serious deviation from linearity or difference between

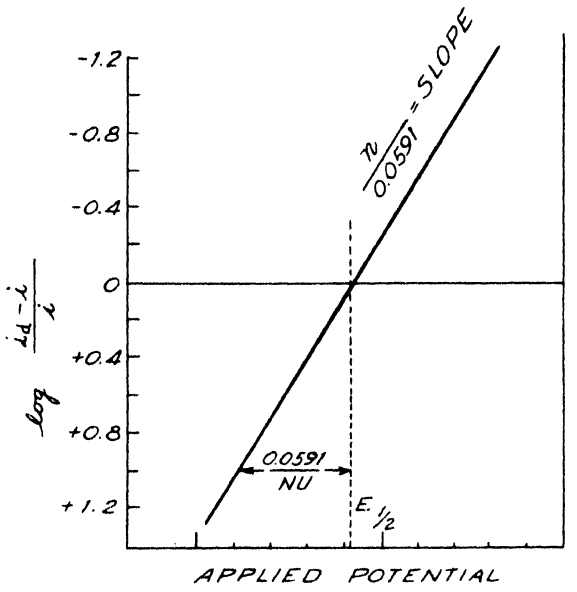

Fig XVI-6. Test of the equation of a typical polarogram for reversibility. Values of half-wave potential ($E_{\frac{1}{2}}$) and number of electrons (n) involved are shown

the actual and theoretical slopes is an indication that the electrode reaction does not proceed reversibly. The best test for reversibility, however, involves determining the half-wave potentials for the anodic, cathodic, and mixed cathodic-anodic polarographic waves of the material. If all three polarograms possess the same half-wave potential, Fig. XVI-7, the electroactive material undergoes reversible oxidation and reduction at the microelectrode.

If the reaction at the microelectrode surface involves complexes, satisfactory polarograms can be obtained only if the dissociation of the complex is sufficiently rapid as compared to the rate of diffusion, so that the concentration of the dissociated ion is maintained constant at the electrode interface. Let us consider a generalized reduction:[13]

$$MX_p^{(n-pb)+} + ne + Hg \rightarrow M(Hg) + pX^{-b} \quad (20)$$

The expression for the electrode potential can be written

$$E_{\frac{1}{2}} = E^o + \frac{0.0591}{n} \log K_{instab} - \frac{0.0591}{n} \log [X^{-b}]^p \quad (21)$$

In these equations p is the coordination number of the complex ion formed, n is the number of electrons involved in the electrode reaction, X^{-b} is the complexing agent, and K_{instab} is the value of the instability constant for the complex

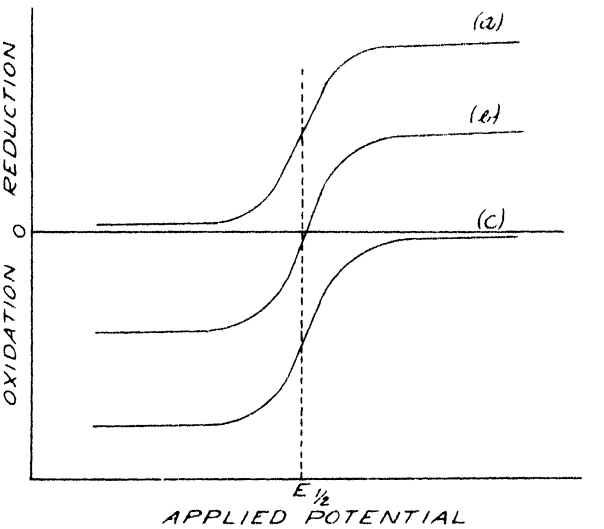

Fig. XVI-7. Schematic representation of polarograms. (a) Cathodic wave of oxidant. (b) Mixed cathodic-anodic wave of a mixture of oxidant and reductant. (c) Anodic wave of reductant

formed. It will be noted in equation (21) that the concentration of the metal-ion complex does not enter into the expression, and hence the observed half-wave potential will be constant and independent of the concentration of the complex metal ion. The extent of the shift of the half-wave potential will be primarily due to the strength of the complex ion formed as evinced in the log K_{instab} term. However, the half-wave potential will also shift with changing concentration of the complex forming agent. Therefore, the half-wave potential is determined at two different concentrations of the complexing agent, and

$$\frac{\Delta E_{\frac{1}{2}}}{\Delta \log [X^{-b}]} = -p \frac{0.0591}{n} \quad (22)$$

Thus the polarographic method could be used for the determination of coordination numbers and

13. For comprehensive treatment, see Lingane, J. J., Chem. Rev., 29, 1 (1941).

for rough approximation of the instability constants of electroactive complex ions.

APPLICATIONS OF POLAROGRAPHY

Scope of Polarography

A large number of substances, both inorganic and organic, which are reducible or oxidizable, give characteristic polarographic waves. For details, the reader is referred to the monograph by Kolthoff and Lingane, or to the bibliographical compilation published by Sargent and Company. A brief résumé of the various classes of substances which are known to yield satisfactory polarograms follows.

Cathodic Waves. Polarograms for a large number of inorganic cations, either in the form of simple ions or in the form of complex ions, have been obtained. Even the alkali and alkaline-earth metals give waves at very negative potentials if tetramethyl ammonium salts are used as supporting electrolytes. Also metals, such as aluminum, not deposited electrolytically under usual conditions, may be determined polarographically since they do form very dilute amalgams. However, waves from easily hydrolyzable and strongly electronegative cations are apt to be masked by the discharge of hydrogen ions.

A considerable number of oxy-anions are reducible in well-buffered solutions. Their half-wave potentials are greatly influenced by the pH of the supporting electrolyte as would be expected, since hydrogen ions are involved in their reductions. These include iodate, bromate, permanganate, nitrite, tellurite, and selenite ions. Nitrate and nitrite ions are reducible in the presence of certain multi-valent ions such as lanthanum, ceric, or uranyl, owing to the formation of loose ion-pairs of the type $La(NO_3)^{++}$.

The reduction of oxygen is important as a method of determining the gas, and also because the oxygen waves interfere with most other cathodic waves. Other uncharged substances which are reducible include sulfur dioxide, nitric oxide cyanogen, hydrogen peroxide, bromine, chlorine, and iodine.

A large number of organic compounds are reducible[14] and give well-defined waves, but since hydrogen ions usually enter into the reduction process, the solutions must be well-buffered. Typical compounds include those with the following substituent groups: Carbonyl, quinone, nitro, nitroso, azo, and most unsaturated compounds with conjugated double bonds.

Anodic Waves. Anodic waves of two types are obtained. With noble metal microelectrodes, polarograms due to the oxidation of ferrous and ferrocyanide ions, and hydroquinone are known. However, when a dropping mercury electrode is employed in solutions containing halide or other ions[15] that form insoluble or complex ions with mercurous ions, the electrode becomes depolarized, and the mercurous anodic wave is shifted to more negative potentials. Especially in strongly alkaline solutions, the depolarizing effect of the hydroxyl ion will interfere in obtaining cathodic waves near zero applied potential.

Catalytic Waves. The high hydrogen overvoltage of mercury is lowered by certain substances, particularly the platinum group metals,[16] which catalyze the evolution of hydrogen on the electrode surface of the dropping electrode at more positive potentials than the normal discharge potential of hydrogen. Proteins and organic compounds containing the sulfhydryl group cause a catalytic wave to appear in the presence of a small concentration of cobalt-ammine ions.[17]

Suppression of Maxima. The suppression of the prominent oxygen maxima by various capillary active substances, such as dyes, lyophilic colloids, fatty acids, and alkaloids, has been used for determining traces of these materials.

Specific Applications

Although a great deal is known concerning the specific behavior of many substances in different supporting electrolytes, very few systematic schemes of quantitative analyses have been devised. Kolthoff and Lingane have summarized the early work in their monograph. Progress is continuing, however; and, principally through the efforts of Lingane and Kolthoff, schemes are now available for the separation and analysis of the metals in the acid hydrogen sulfide group,[18] the constituents of copper-base alloys,[19] and the

14. Muller, O. H., Chem. Rev., 24, 95 (1939). Compilation through 1938.

15. Revenda, J., Coll. Czeck. Chem. Commun., 6, 453 (1934); Kolthoff, I. M. and Miller, C. S., J. Am. Chem. Soc., 63, 1405, 2732 (1941).

16. Slendyk, I., Coll. Czeck. Chem. Commun., 4, 335 (1932).

17. Brdicka, R., ibid., 5, 112, 148, 238 (1938).

18. Lingane, J. J., Ind. Eng. Chem., Anal. Ed., 16, 147 (1944).

19. Ibid., 18, 429 (1946).

constituents of aluminum-base alloys.[20]

Reducible tank gases can be analyzed by measuring their diffusion waves after saturating the supporting electrolyte by bubbling the gas through the solution. The residual current of the supporting electrolyte is determined beforehand.

The polarograph has played an important role in investigation of a theoretical nature and perhaps should be resorted to oftener when conventional methods fail. For example, it has been used as a pilot technique to determine the optimum conditions under which reductions with the mercury cathode should be conducted, as in the reduction of acridine compounds[21] or in the deposition of various metals using controlled cathode potentials.[18] The effect of substitution in an organic molecule upon its reduction potential has been extensively studied by Shikata and Tachi,[22] who found a correlation between the ease of reduction polarographically and the Raman and absorption spectra of the compounds as more electronegative groups are substituted in the compound. Other fields of study have included reaction kinetics (inversion of cane sugar, Cannizzaro reaction, molecular rearrangements), polymerization of formaldehyde and pyruvic acid, and tautomerism, to mention only a few. The possibilities of determining the coordination number and a rough value of the instability constants of various complexes has already been discussed, as has the method for determining the number of electrons involved in the electrode reaction.[23]

Quantitative Technique. Polarographic analyses are carried out most easily if the electroactive material is present in a concentration of 10^{-4} to 10^{-3} molar, and in a solution whose volume is between 10 and 50 ml. However, concentrations as large as 0.01 M or as small as 10^{-6} molar, and volumes as small as one drop can be analyzed in extreme cases. The lower limit of concentration might be extended if a rotating microelectrode could be employed. For the latter instances special precautions are necessary and the accuracy diminishes. Individual analyses are usually precise to about 5%, but strict adherence to technique and limiting conditions can reduce the uncertainty of duplicate analyses to about 2%. These factors have been analyzed and a set of tolerances established which permit such a precision to be realized in practice.[24]

It has been mentioned that oxygen dissolved in the polarographic solution is reducible, the wave starting about -0.4 volt vs. S.C.E. Therefore, it is necessary to remove any dissolved oxygen from the electrolytic solution whenever cathodic regions of potentials are being investigated at which oxygen interferes. This is accomplished simply by bubbling an inert gas through the solution for about 15 minutes before determining the current-voltage curve. Hydrogen gas, or nitrogen gas, purified by passage over heated copper gauze or through either chromous chloride or alkaline pyrogallol, is usually used. During the actual course of the measurements, the gas stream must be discontinued to prevent its stirring effect from interferring with the diffusion process near the microelectrodes, or with the formation of drops of mercury of normal size. In neutral or alkaline supporting electrolyte, the oxygen is quickly and simply removed by the addition of a small amount of solid sodium sulfite. The solutions should be protected from contact with air by allowing a stream of the inert gas to pass over their surface while the polarogram is being recorded.

Stirring is permissible when solid microelectrodes are used as long as the stirring is uniform and no turbulance exists at the electrode surface. A sufficient amount of liquid will always cling to the electrode surface to provide a uniform diffusion layer.

The effect of temperature upon the diffusion current with different indicator electrodes has already been discussed. A thermostat regulated to within a 0.25°C. is desirable for analytical work. The electrolytic cell should be immersed in a constant temperature bath during the period required for the removal of oxygen so that thermal equilibrium will be reached throughout the solution; otherwise, convection currents will disturb the diffusion process.

Enough gelatin to give a final concentration of 0.005% to 0.01%[25] should be added to the supporting electrolyte as a precautionary measure to prevent the appearance of maxima. The gelatin solution should be made fresh each day unless

20. Kolthoff, I. M. and Matsuyama, G., Ibid., 17, 615 (1945).

21. Lingane, J. J., Swain, C. G. and Fields, M., J. Am. Chem. Soc., 65, 1348 (1943).

22. Shikata, M. and Tachi, I., Coll. Czeck. Chem. Commun., 10, 368 (1938).

23. Cf. coulometric method of analysis.

24. Buckley, F. and Taylor, J. K., Trans. Am. Electrochem. Soc., 87, 197 (1945).

25. Buckley, F. and Taylor, J. K., J. Res. Natl. Bur. Stds., 34, 97 (1945).

the operator has mastered the technique of preserving the solution from bacterial action. Even so, the gelatin will only last a few days.

Removal of Interferences. Two electroactive ions may be determined successively if their half-wave potentials are separated by at least the factor 0.0591/n log 1000, or about 0.35 volt for univalent ions and 0.2 volt for bivalent ions, and if the ions are present in concentrations that are approximately equal. If the latter condition is not true, the separation of the half-wave potentials must be correspondingly larger.

For materials containing two substances with overlapping or interfering waves, either of two procedures may be adopted to remove one of the ions. Sometimes the half-wave potentials of one of the interfering ions may be shifted to more negative potentials by taking advantage of certain complexing agents, which are incorporated in the supporting electrolyte, similar to the procedures utilized in ordinary electrolytic depositions. Occasionally the interfering ion may be satisfactorily removed by ordinary precipitation techniques, although the possibilities of adsorption or coprecipitation of part of the other ions must always be borne in mind.

Oftentimes in polarographic work the difficulty centers about a nobler ion which is predominant in the unknown material. Consequently, the galvanometer sensitivity cannot be increased to magnify the current-voltage curve of any minor constituents, since the magnitude of the preceeding wave due to the nobler ion is also correspondingly enlarged. The second of the two previously mentioned procedures might be employed to remove the bulk of the nobler ion, but the large amount of precipitate which would have to be handled, plus the danger of removing some of the minor constituents by adsorption or coprecipitation, detracts from the procedure.

Lingane has proposed an elegant procedure[18] when one or more of the nobler metals of a group predominates and thus interferes with the polarographic determination of the remainder. The interfering elements are removed by electrolysis with a mercury cathode at a carefully controlled potential, and the minor base metals are then determined in the residual solution. A mercury cathode is uniquely advantageous for this type of electrolytic separation because the optimum values of the limiting cathode potential may be deduced reliably from the known polarographic characteristics of the metals to be separated. In some instances a platinum gauze cathode could be used equally satisfactorily.

Another method which may be used to remove the interference of large amounts of nobler metal ions, if the waves are well-defined and considerably removed from each other, is to employ the compensator-condenser technique suggested by Lingane and Kerlinger.[26] The compensator is an auxiliary battery and potential divider arrangement designed to impress an opposing e.m.f. across the galvanometer shunts just equal to the e.m.f. generated by the interfering diffusion current. In addition a high capacitance condenser must be connected across the galvanometer terminals to decrease the magnitude of the galvanometer oscillations. These are correspondingly enlarged when the sensitivity is increased to magnify the diffusion current of the less noble ion. This method may be used satisfactorily up to a concentration ratio of the major to minor constituent of about fifty to one.

Evaluation of Quantitative Results. Taylor,[27] in a recent review, has discussed the merits of the various methods in use for evaluating results, and much that follows will be taken from his paper.

All the early work made use of the polarograph as an interpolative device in that the determination depended upon the comparison of the heights of the waves found for standard and unknown solutions. The precision of such methods increases, the greater the correspondence of the composition of the unknown and known and the physical conditions of the analysis. The limiting factors are the reproducibility of the waves and the precision with which the intercomparison of wave heights may be made. The latter is nearly independent of the method of measurement, provided similar procedures are used for both the unknown and the standard solution. Some of these are briefly described below.

Wave Height - Concentration Plots. This method is perhaps the simplest to use. Solutions of several different concentrations of the ion in question are prepared using identical amounts of supporting electrolyte, and the heights of the waves obtained are measured in any convenient manner and plotted as a function of the concentration. The unknown is run and measured exactly as the standards, and the concentration is read from the graph. The method is strictly empirical, and, although frequently true, the wave height

26. Lingane, J. J. and Kerlinger, H., Ind. Eng. Chem., Anal. Ed., 12, 750 (1940).

27. Taylor, J. K., Anal. Chem., 19, 368 (1947).

need not be a linear function of the concentration. For best results the unknown should be bracketed by standard solutions run concurrently, in which case no other polarographic method gives higher precision.

Pilot-Ion Method. Forche[28] originally described this method which depends upon determining the relative wave heights of the unknown ion and some standard ion added to the solution in known amount, the ratio of wave heights for known amounts of the two ions having been determined by a previous calibration. This ratio of relative diffusion currents of the "pilot" ion and another ion in the same supporting electrolyte will always be independent of characteristics of the capillary electrode, and of temperature to a close approximation. However, it has had limited application because only a small number of ions are available to act as pilot or reference ions and because in multicomponent mixtures there is seldom sufficient difference between half-wave potentials to introduce additional waves.

Method of Standard Addition. Two procedures may be used wherein additional amounts of the ion to be determined are added to a solution for the determination of the relationship between the wave height and concentration. In the first, the polarogram of the unknown is recorded, after which a known volume of a standard solution of the same ion is added to the cell and a second polarogram is taken. From the magnitudes of the two waves - where H is the height of the combined waves, and h, that of the unknown alone; n, the known volume in milliliters of ion added whose concentration is C; and m, the volume of the unknown solution - the concentration of the unknown is readily calculated from the equations given by Müller.[29]

$$X = Kh \tag{23}$$

$$\frac{mX + nC}{m + n} = KH \tag{24}$$

$$X = \frac{-nCh}{mh - H(m + n)} \tag{25}$$

The second procedure consists in adding a known quantity of the substance sought to the unknown before processing, and subjecting this combined sample to the same treatment as the unknown separately. The amount of the unknown is then determined from equation (26):

$$X = \frac{nCh}{m(H - h)} \tag{26}$$

Absolute Method. The absolute method of polarographic analysis makes use of the Ilkovic equation for the evaluation of the concentration of electrolyzable ion. Until recently the general application of this equation was hindered by the unavailability of precise values for the diffusion coefficient of most electrolyzable ions under the conditions of electrolysis. Recently the utility of the Ilkovic equation was greatly enhanced by the following proposal of Lingane.[30] Since n and D are constants for a given electroactive ion in a given supporting electrolyte at a given temperature, and k is a constant independent of the system investigated, he suggested that these three terms be combined into one constant, henceforth to be called the "diffusion current constant," such that

$$I = knFD^{1/2} = \frac{i_d}{Cm^{2/3}t^{1/6}} \tag{27}$$

Thus the unknown ion concentration can be readily determined from a single calibration experiment. In addition to a knowledge of the diffusion current constant, this method requires that the quantity $m^{2/3}t^{1/6}$ be known for the particular capillary that is employed; but the determination of these quantities requires only a very few minutes of time. Tables of diffusion current constants for various supporting electrolytes are becoming increasingly available (see the Appendix).

This latter method is the only reliable means of making an experimental procedure directly available to a potential user without the necessity of performing standardization experiments for himself. Serious errors will arise in the use of the method if the boundary conditions under which the Ilkovic equation was derived are departed from or if irregularities occur in the behavior of a particular solution. Buckley and Taylor[24] in another paper have discussed the precision which may be expected in the measurement of the various terms in the Ilkovic equation.

28. Forche, H. E., Microchemie, 25, 217 (1938).

29. Müller, O. H., "Polarographic Method of Analysis," Mack Printing Co., Easton, Pa., 1941, p. 88.

30. Lingane, J. J., Ind. Eng. Chem., Anal. Ed., 15, 583 (1943).

DIRECTIONS FOR PREPARATION OF EQUIPMENT AND SOLUTIONS

Dropping Mercury Electrode Assembly. The working area for the dropping electrode and cell assembly should be provided adjacent to the instrument. Generally the assembly consists of a mercury reservoir, a connecting tube between the reservoir and the dropping capillary, and a small glass electrolytic cell in which the unknown solution is contained. The mercury reservoir is usually a 125 ml. leveling bulb. The connecting tube between the reservoir and the capillary may be either heavy wall rubber tubing or a glass tube, 80 cm. in length with 10 to 15 mm. diameter, with a stopcock on the lower end and connected to both the reservoir and capillary with short lengths of rubber tubing. The latter type assembly has been found satisfactory by the authors. A sketch of the assembly is given in Fig. XVI-8.

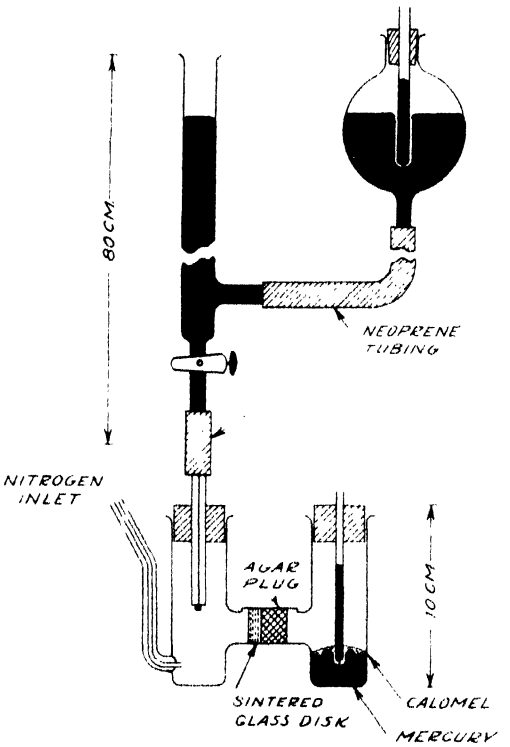

Fig. XVI-8. The dropping mercury electrode assembly with an H-type cell. (After Lingane and Laitinen)

The rubber tubing used in the assembly must be a good grade, handmade variety. Before use, it must be treated 24 hours with a hot, 10% sodium hydroxide solution, then thoroughly rinsed with distilled water, and dried. This is done to remove any traces of sulfur and other surface impurities. If neoprene tubing is used, clean the inside by steaming for a half-hour followed by air drying through a cotton plug filter. If a stopcock is used, it should be adequately wired to withstand the pressure of the mercury above it, and very lightly greased on both sides of the bore; but no grease should be allowed to contact the mercury. Only doubly distilled mercury should be used. Filter the mercury through a filter paper cone with a small hole punched in the tip, before placing it in the reservoir, in order to remove any surface oxides or dust.

The economical use of mercury requires conservation and recovery of any initial amount put into service. When the polarographic cells are emptied, the entire contents, including mercury and liquid, should be thrown into a collecting jar; and, when accumulated in sufficient quantity, this mercury should be washed with water and then agitated overnight in contact with 10% nitric acid solution. A plain gas washing bottle, arranged to admit air through the bottom of the mercury when the outlet is connected to a water aspirator, serves admirably. Then the mercury is washed thoroughly with water, dried with pieces of filter paper, and twice distilled under reduced pressure.

Capillary pyrex tubing possessing a bore diameter in the vicinity of 0.05 mm. is used in 6 to 8 cm. lengths, with the delivery tip cut accurately horizontal. A satisfactory brand is barometer tubing from Corning Glass Works, Corning, N.Y., or it may be purchased from any manufacturer of commercial polarographs. The drop time should lie between 3 and 4 seconds per drop, under a constant head of mercury. If varying the mercury head does not bring the drop time within 3 or 4 seconds per drop, the capillary should be discarded and another substituted in its place.

If the capillary is treated carefully, it will remain serviceable for many months. When not in use, it should be kept immersed in distilled water. Always start the flow of mercury from the capillary before removing it from the distilled water, and never stop the flow after an analysis is finished until the tip has been thoroughly rinsed and returned to the distilled water vessel. Some liquid will always be drawn up into the capillary bore after the mercury flow has ceased. However, if the capillary does become plugged, treatment with 20% nitric acid solution may slowly dissolve the contamination within the bore.

When the dropping mercury electrode is used and the results are to be computed by the absolute

method of Lingane, the mass of mercury per second flowing through the capillary must be determined. The special style cell[8] used by Kolthoff and Lingane may be used, or the mercury drops may be simply collected under distilled water in an ordinary small weighing bottle. In either case the mercury head must be adjusted to the same height that will be used during the course of the analyses. Collect approximately twenty drops and measure the time interval with a stopwatch, remove the water with a medicine dropper, rinse with acetone, and dry for a few seconds in an air jet, then weigh.

Solid Microelectrode Assembly.

Various styles of stationary platinum electrodes have been tested by Kolthoff and Laitinen,[4] who recommend a 3 mm. length of straight platinum wire, 0.05 mm. in diameter, projecting down from a glass tube. Two types of rotating platinum microelectrodes have also been described by Kolthoff and Laitinen,[31] differing from the stationary in that the platinum wire projects from the side of the glass tubing. Electrical connection to the electrodes is made by means of a piece of copper wire dipping into a pool of mercury inside the tubing.

A motor rotating uniformly at about 600 r.p.m. is used for experiments involving rotating electrodes. A Cenco cone-drive motor is satisfactory. The external wire leading from the microelectrode is allowed to make contact with the motor's chuck. Any external circuit can then be connected from any point on the motor frame. If proper contact through the motor frame is impossible, a flanged reservoir can be built onto the glass tubing into which the external connections are then made independently of the motor chuck.

Electrolysis Cells

Polarographic cells are many and varied; generally each user has his own special type. Whatever the style, provision must be made for bubbling the inert gas through the solution and making contact with the mercury pool if it is used as anode. Lingane and Laitinen recommend an H-type cell which contains a calomel reference electrode in one side separated by an agar plug from the solution.

Reference Electrodes

If the mercury pool is to be dispensed with, and an external electrode used in its place, the surface area of the external electrode should be approximately 10 sq. cm. A large size test tube with side arm and stopcock attached, or an ordinary 50 ml. Erlenmeyer flask, may be used to contain the standard calomel electrode. Connection is made to the electrolytic cell by means of a salt bridge filled with a saturated solution of potassium chloride, ammonium nitrate, or potassium nitrate.

Purification of the Inert Gas

Tank gases of nitrogen or hydrogen usually contain traces of oxygen which must be removed before they are bubbled through the test solution. Oxygen can be removed from the tank gases by passing the gas through either a heated tube filled with copper turnings or a washing bottle filled with a solution of chromous chloride, alkaline hydrosulfite containing anthraquinone-beta-sulfonate, or alkaline pyrogallol. Specific directions for the preparation of the aqueous absorbents and the temperature ranges for the solid reactants will be found in any text dealing with gas analytical methods. Regardless of which method is chosen for removing oxygen, the gas is next passed through a washing bottle filled with the same type solvent used for the test solution so that the gas stream will become saturated and thereby prevent undue removal of the test solution, and also to remove any spray which may carry over from the liquid absorbents.

Thermostat.

Where accurate determinations are to be made, the polarographic cell must be maintained at $25.0^{\circ} \pm 0.25^{\circ}$ C. An electrically controlled, automatically heated laboratory water bath can easily be assembled. If the electrode assembly is considerably removed from the bath, a circulafing pump may be used to provide adequate circulation to a small trough equipped with an ample overflow return.

Preparation of Gelatin

A gelatin solution is added to the supporting electrolyte as a precautionary measure. Weigh out 0.200 g. of powdered gelatin on an analytical balance and dissolve in 100 ml. of distilled water which has been previously boiled for 10 minutes and then cooled to 50° or 60° C. Add a few drops of toluene to the solution and stopper firmly with a sterile rubber stopper. All the operations are carried out in the flask in which the gelatin solution eventually will be stored. Properly prepared and stored, the gelatin solution will usually keep for several days. As soon as bacterial action is suspected, fresh gelatin

31. Laitinen, H. A. and Kolthoff, I. M., J. Phys. Chem., 45, 1079 (1941).

must be immediately prepared.

Preparation of the Unknown Solution

The concentration of solutions suitable for polarography should lie between 10^{-3} and 10^{-5} normal. Larger concentrations will be of no avail as the galvanometer sensitivity must be correspondingly decreased. If the concentration of a sample is not known, an exploratory run should be made to secure an idea of the approximate concentration. The unknown sample, or a suitable aliquot, is transferred to a volumetric flask. A sufficient amount of supporting electrolyte to give a final concentration of 0.1 to 0.2 normal is added. Enough gelatin is added from a pipet to make the final concentration 0.005% to 0.010%, and the entire solution diluted to the mark.

Fill the electrolytic cell with enough solution to surround the solid microelectrode or the capillary tip of the dropping mercury electrode. Cover the bottom of the cell with a layer of mercury unless an external reference electrode is used. (Use a tray under all vessels containing mercury and for all operations involving the transfer of mercury. Mercury vapor is definitely poisonous and has an appreciable vapor pressure, and spilled mercury is difficult to recover.) Place the entire electrolytic cell and electrode assembly in the thermostat regulated to $25.0^{\circ} \pm 0.25^{\circ}$ C. Remove all reducible dissolved gases by bubbling an inert gas stream through the solution for 15 to 20 minutes prior to taking the polarogram. Discontinue the inert gas stream while the polarogram is being recorded.

If an alkaline supporting electrolyte is to be used, and no lead ions are present in the solution, add enough sodium sulfite to make the final concentration 1%; then allow 10 minutes for the dissolved oxygen to be reduced before recording the polarogram.

DIRECTIONS FOR THE OPERATION OF THE SARGENT POLAROGRAPH MODEL XII

Circuit Diagram and Description of Functional Components.

The basic circuit for the photographically recording Sargent polarograph is shown in Fig. XVI-9. Observe Fig. XVI-10 also. Essentially it consists of a uniform slide wire (scale ring reading s) around a drum, connected by a set of gears to a cylinder housed in a light-tight compartment and carrying a sheet of photographic paper. The potential drop across the slide wire is adjusted to any

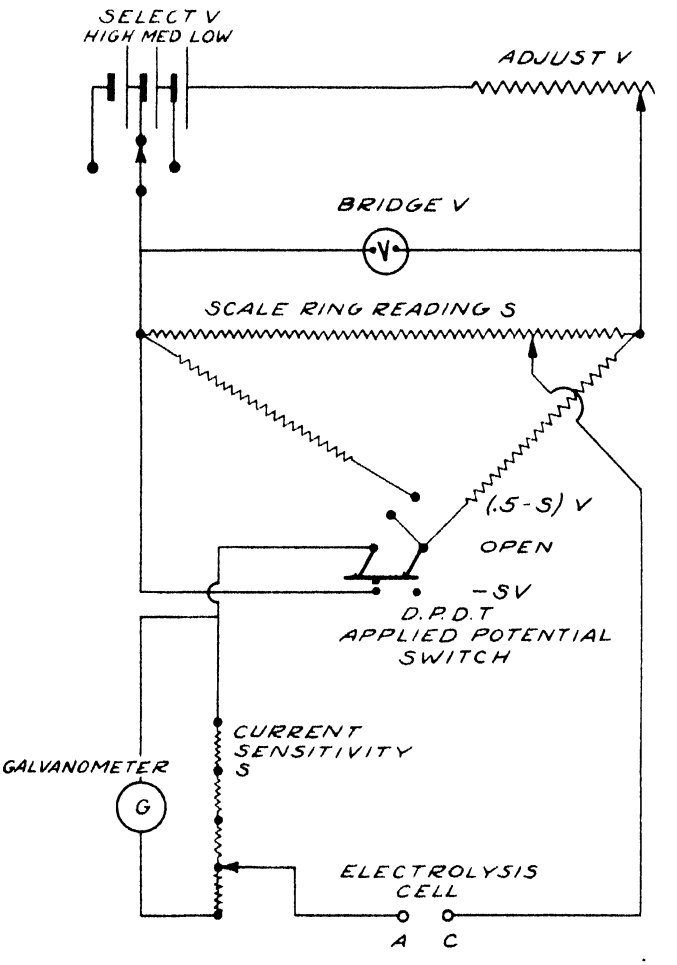

Fig. XVI-9. Circuit diagram of the Sargent Polarograph Model XII

desired value (BRIDGE V) by selecting (SELECT V) one, two, or three dry cells in series and regulating the voltage by means of a series resistance (ADJUST V). The drum carrying the slide wire is rotated either manually or by means of an electric motor (MOTOR), and as it revolves a continually increasing e.m.f. is applied to the electrolysis cell (AC). G is a sensitive d'Arsonval galvanometer, (10^{-9} amp./mm.), which possesses a long period (15 seconds), the light beam of which is reflected onto both the photographic paper and to a visual scale on the front of the instrument case. The housing of the photographic cylinder is provided with a narrow collimating slit, which can be opened or closed by a shutter on the revolving drum assembly and through which the light beam of the galvanometer enters.

A reversing switch (APPLIED POTENTIAL) is provided to allow anodic or cathodic voltages to be applied to the microelectrode. In the left-hand (.5 - S)V position, a shunt is connected by means of which one electrode

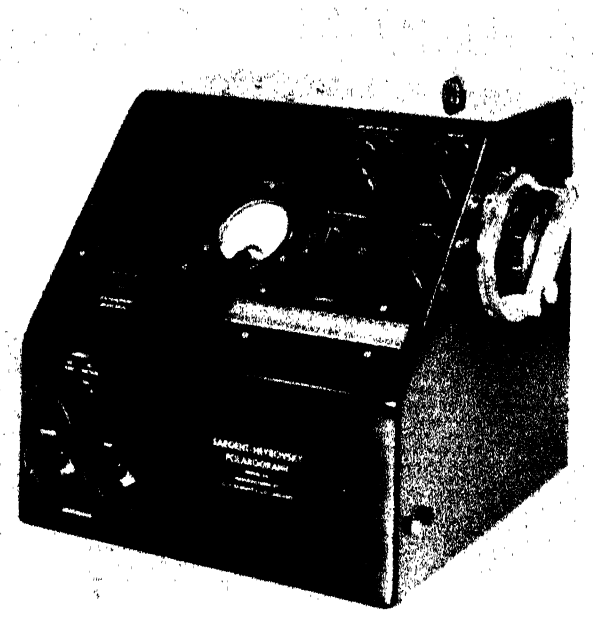

Fig. XVI-10. Heyrovsky Polarograph Model XII (Courtesy of E. H. Sargent & Co.)

may be connected to the middle of the slide wire allowing the other electrode to pass from positive through zero to negative applied potential values as the slide wire is advanced from 0 to 1.0, or vice versa. In the right-hand (-SV) position, the slide wire is connected so as to apply a gradually increasing potential from zero to the maximum value given by the voltmeter (BRIDGE V).

The current sensitivity knob is an Ayrton shunt in parallel with the galvanometer. The readings indicate the fraction of the total current actually passing through the galvanometer.

Loading the Camera

Detach the camera by turning the lock-handle toward the center to un-lock, then pull out the camera assembly by the outer, chromium plated ring, after assuring yourself that the shutter is closed. The shutter is operated by the small chromium plated knob on the outer ring of the camera.

In the darkroom, using a red or light green safelight for bromide papers, pull the paper holder out of the outer case, loosen the locking bar by pressure from the inside of the cylinder. If there is a polarogram on the drum, put it away in a black envelope. Take a sheet of 6" x 10" bromide paper,[32] smooth it around the cylinder of the camera, emulsion side to the outside, so that the edge touches the guide bar all the way around, tuck the ends into the long slot, and lock the locking bar by pressing it firmly into the slot. Slip the camera back into the case. Make sure that the shutter is closed. The camera is now ready to be slipped back into the polarograph, the shutter at the top. Turn the locking handle toward the outside.

Instrument Operation

Place the power plug into a 110 volt, 60 cycle line. Insert the leads from the polarographic cell into their respective jacks on the right-hand side of the instrument, the red is positive, black is negative. For most purposes the black is connected to the microelectrode and the red is connected to the pool or external reference electrode.

Turn the switch marked LAMP to the ON position. Bring the galvanometer light on the front instrument panel to zero by adjustment of the galvanometer zero on the top of the instrument housing.

Turn the SELECT V switch to the appropriate voltage range, which can be read on panel voltmeter (BRIDGE V), and make the fine adjustment of the voltage with the ADJUST V switch. The voltmeter reading indicates the total voltage drop across the slide wire from 0.0 to 1.0 divisions.

Rotate the camera-slide wire drum to the zero position. If cathodic voltages are to be used, turn the applied potential switch to the right-hand (-SV) position. The left-hand setting (.5 - S)V of this switch is provided for obtaining anodic voltages, in which case the slide wire will read from +0.5 through zero to -0.5 volts when the voltmeter reads 1 volt, or +1.0 through zero to -1.0 volts when the voltmeter reads 2 volts, etc.

Set the current sensitivity knob to the desired value; 50 is a safe exploratory value to begin with. Slowly rotate the camera assembly manually and observe the galvanometer light. If full-scale deflection is not obtained, increase the sensitivity of the galvanometer by turning the CURRENT SENSITIVITY knob to a smaller value.

When the voltage range and the current sensitivity of the polarographic wave have been established, move the slide wire one-tenth of the slide wire distance back from the potential at which the wave commences, release the locking lever, and rotate the camera holder position "1" until opposite the engraved mark, lock the camera holder, open the shutter, and turn the motor switch ON. After the slide wire has been advanced to the maximum voltage which is to be recorded (usually one tenth of the slide-wire distance after the current rise ceases - that is, after the current plateau commences),

32. Kodabromide F-1 and Kodak Royal Bromide E-1; du Pont Defender Velour R-1 is slower but satisfactory.

close the shutter, and turn OFF the motor. After setting the slide wire by hand to the next starting voltage, loosen the locking handle, set the camera holder to position "3," lock the camera holder, and record the second polarogram in the same manner. Succeeding camera positions are determined by the extent of the preceding polarograms, but usually positions "5" and "7" can be used for succeeding curves.

Take the camera to the darkroom and develop the paper for 1-2 minutes in D-72 developer (using the same safelight as before), rinse the paper in water for a few seconds, and fix it in F-1 fixing bath for 15 minutes, agitating a few times. Wash in running water for 30 minutes and dry between blotters or, better, press on a ferrotype tin.

Use of the Compensator.

If it should become advantageous to apply a potential in the galvanometer circuit which is in opposition to that arriving from the electrode system in order to balance out a large diffusion wave preceding a smaller one of a less noble ion, the compensator control may be used. The potential is adjusted to the value at which the interfering diffusion current wave is completely developed, then the compensator control is turned ON and the voltage knob rotated until the galvanometer light is brought to zero or to the previous diffusion current plateau or residual current, whichever it may be. If the galvanometer light cannot be returned to the desired position, turn the compensator current knob until it does. The galvanometer sensitivity may then be increased and the analysis continued in the usual way. It is important to return the compensator control to the OFF position after use.

DIRECTIONS FOR THE OPERATION OF THE FISHER ELECDROPODE

Circuit Diagram and Description of Functional Components.

The Fisher Elecdropode is a manually operated instrument whose basic circuit is shown in Fig. XVI-11. Observe Fig. XVI-12 also. Its operating potential is supplied by a set of three dry cells which are standardized before use against an Eppley Standard Cell. R_1 in the diagram is represented by the knob STD. A set of end coils used in conjunction with the slide wire (POTENTIAL) permits selection of one-volt ranges between 0 - 1V, 1 - 2V, or 2 -3V with the functions ganged switch. The potential dial is moved manually to supply a continually increasing e.m.f. to the electrolysis cell (DROP POOL). G is a sensitive d'Arsonval galvanometer (10^{-8}

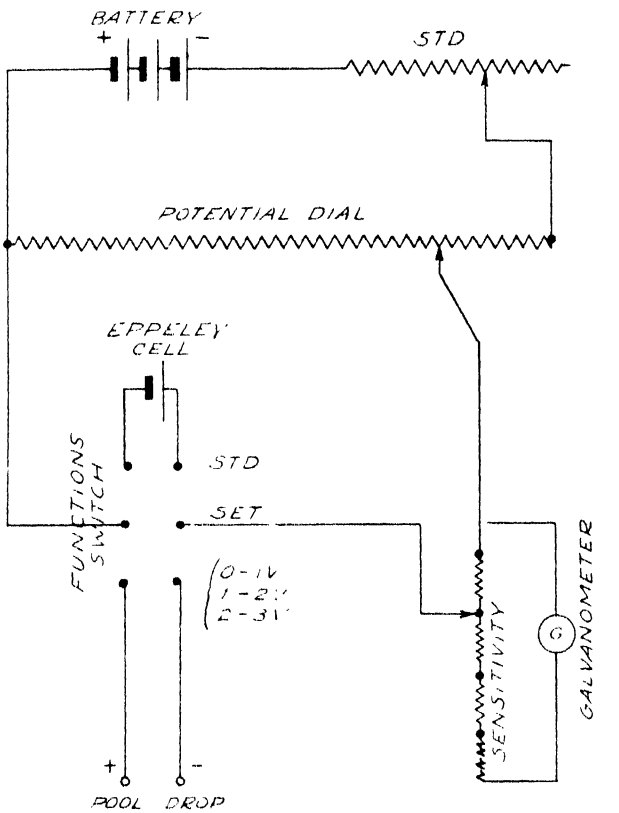

Fig. XVI 11. Schematic circuit diagram of the Fisher Elecdropode

amp./mm.) which possesses a long period, the light beam of which is reflected onto a visual scale across the top of the instrument panel.

A reversing toggle switch (+ -) is provided to allow anodic or cathodic voltages to be applied to the microelectrode. The POOL potential may be determined by measuring it against a standard calomel half-cell when the functions switch is placed at CAL, or a standard external reference half-cell may be connected in place of the pool lead.

Inside the instrument case is a condenser, C, to decrease the galvanometer oscillations; some instructors may wish to remove it since its presence tends to cause the galvanometer to overshoot or undershoot its equilibrium period, whereas the actual oscillations are never bothersome with the lower sensitivity of the instrument's galvanometer, as compared to the Sargent instrument.

The sensitivity knob is an Ayrton shunt in parallel with the galvanometer, and whose readings indicate the fraction of the total current actually passing through the galvanometer.

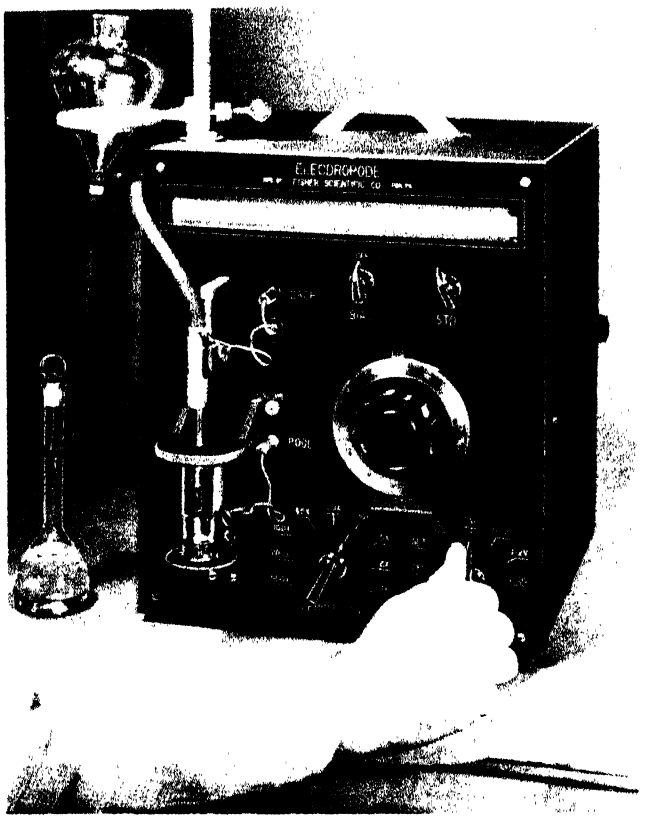

Fig. XVI-12. Elecdropode (Courtesy of Fisher Scientific Co.)

Instrument Operation

Insert the power plug into a 110 volt, 60 cycle line. On the back of the instrument will be found two binding posts for attaching an external galvanometer and a toggle switch for switching from "I" (Internal) to "E" (External) galvanometer. With the toggle switch in the external position the galvanometer shunts remain in the circuit.

Adjustment of Galvanometer Index. Turn the functions switch to SET, which turns on the galvanometer light. Bring the galvanometer index to zero by means of the knob on the rear right-hand side of the instrument case.

Standardization of the Working Battery. Turn the functions switch to STD and the sensitivity switch to 5. Bring the galvanometer index to zero by adjustment of the knob marked STD. The potential slide wire has now been calibrated against a Weston cell.

Measurement of Saturated Calomel Electrode Pool Potential. Turn the functions switch to CAL., set the "+ -" toggle switch to Minus, and sensitivity switch to 20. Bring the galvanometer index to zero by rotation of the potential dial. When the index comes to zero read the potential dial and compute the potential of the saturated calomel reference electrode with respect to the pool from the equation:

$$\text{Potential} = 0.004\ (50 - R)\ \text{volts}$$

A negative result indicates that the calomel electrode is negative with respect to the pool and vice versa. In most work this step can be omitted.

Determination of the Polarogram. With the potential dial at zero, set the functions switch to 0 -1 volt. Proceed to increase the potential in small steps of 0.01 to 0.02 volt by rotation of the potential dial and record the maximum oscillation of the galvanometer each time. When the potential dial has been turned to 100, return it to zero and advance the functions switch to 1 - 2 volts. Continue to increase the potential in steps by turning the potential dial. Record the current as the ordinate on graph paper against the potential as abscissa. The total applied potential at any setting is the sum of the settings of the potential dial and the functions dial reading.

Use of the Bias Control. (cf. diffusion current compensator). If it should become advantageous to apply a potential in the galvanometer circuit which is in opposition to that arriving from the electrode system in order to balance out a large diffusion wave preceeding a smaller one of a less noble ion, the bias control may be used. The potential is adjusted to the value at which the interfering diffusion current wave is completely developed, then the bias control is turned on and the knob rotated until the galvanometer index is brought to zero or to the previous diffusion current plateau or residual current, whichever it may be. The galvanometer sensitivity may then be increased and the analysis continued in the usual way. It is important to return the bias control to the OFF position after use.

DESCRIPTION OF A HOMEMADE POLAROGRAPH

Circuit Diagram

However convenient it may be to have available a completely assembled and self-contained instrument, a homemade polarograph nevertheless will give equally reliable and accurate curves. Therefore, an instrument will be described which can be assembled from materials

readily available. Only a sensitive galvanometer (10^{-8} or 10^{-9} amp./mm.) need be purchased.[33] The lamp and scale type manufactured by Rubicon or General Electric give adequate sensitivity. This apparatus is well suited for amperometric titrations, discussed in the following chapter.

The simple circuit is illustrated in Fig. XVI-13.

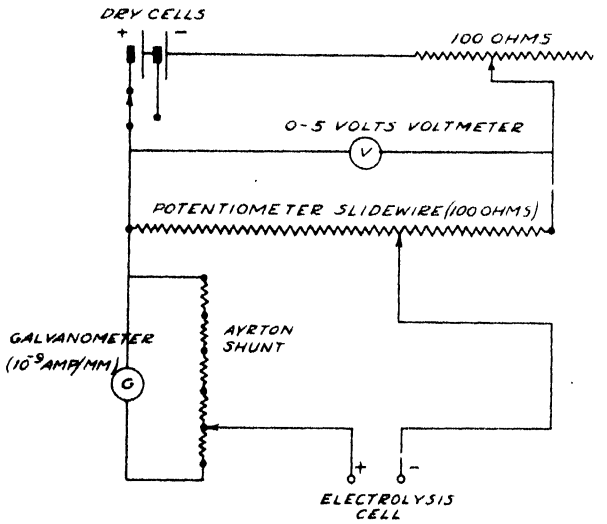

Fig. XVI-13. Simple circuit for obtaining current-voltage curves manually

A suitable potential divider is a Leeds and Northrup potentiometer slide wire of 100 ohms resistance. The potential drop across the slide wire is adjusted to any desired value by inserting one or two dry cells (switch S_1) in series and regulating the voltage by means of a series resistance R_1, a 100 ohm decade resistance box or radio potentiometer. The potential drop across the slide wire is conveniently measured with an ordinary 0 - 5 volt voltmeter, V. The galvanometer shunt, R_2, could be a decade resistance box of 10,000 ohms with a movable center tap, or a Fisher Ayrton shunt.[34] If desired, a reversing switch, not shown, could be inserted to allow the use of anodic potentials, and further modifications made at the instructor's discretion.

MEASURING THE DIFFUSION CURRENTS

Extrapolate the initial residual current curve, or preceding diffusion current plateau, and draw a line parallel to it through the peaks of the succeeding diffusion current plateau as shown in Fig. XVI-14. Measure the rise in millimeters or scale divisions (if plotted manually) for each ion to be determined. The diffusion current in microamperes is given by the equation:

i_d = [deflection in millimeters (or scale divisions)] X [current sensitivity setting (R)] X [galvanometer sensitivity in microamperes per millimeter (or scale divisions)]

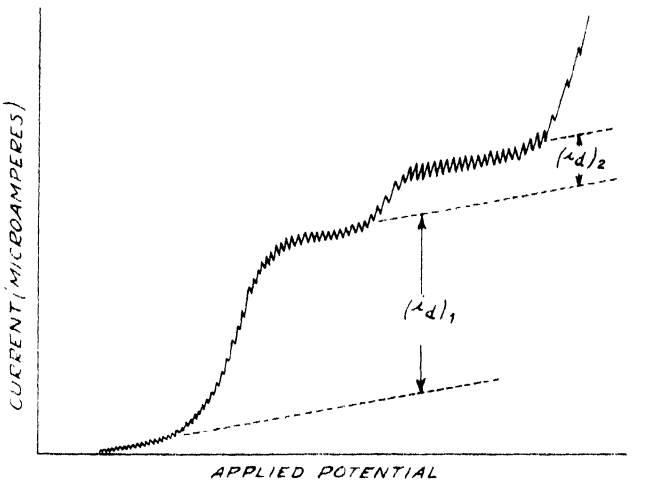

Fig. XVI-14. Method for measuring wave heights

The galvanometer sensitivity will either be stamped on the front panel of the instrument or may be obtained from your instructor. Kolthoff and Lingane have described a simple method for determining galvanometer sensitivities in their monograph.[35]

Some instructors may wish to measure the average current instead of the maximum value. It matters little which method is used as long as the method is followed consistently, except when damping is used. In the latter case average currents should be measured.

ANALYSIS OF A POLAROGRAPHIC WAVE OF CADMIUM

Procedure. To a 100 ml. volumetric flask, add 20 ml. of 1 N potassium chloride solution, 2.50 ml. of a 0.2% gelatin solution, and 10 ml. of a 0.01 N cadmium salt. Dilute the solution to the mark. Transfer a portion of the solution to

33. Cost - approximately 60-100 dollars.
34. Cost - 15 dollars.
35. Kolthoff, I. M. and Lingane, J. J., "Polarography," Interscience Publishers, Inc., New York, 1941, pp. 227-229.

the electrolytic cell, remove the dissolved oxygen, and allow temperature equilibrium to be attained in a thermostat.

After 15 minutes, insert the electrolytic cell under the dropping mercury electrode assembly. Be sure the capillary tip is completely immersed. Manually plot the current-voltage curve between -0.40 to -0.80 volt versus the S.C.E. in increments of 0.01 volt. Extrapolate the residual current curve and draw parallel to it a line through the diffusion current plateau. Measure the height of the diffusion wave, after correction has been made for the residual current, at each increment of applied voltage. It is proportional to the activity of the cadmium amalgam formed; that is, $i = [Red]_i = a_{Cd(Hg)}$. The subtracted difference between the total diffusion current, after correction has been made for the residual current, and the diffusion current at each increment of applied voltage is equal to the concentration of the oxidant or, in this case, the cadmium ions: $(i_d - i) = [Ox]$. On a piece of semilog graph paper, plot the value of $(i_d - i)/i$ versus each increment of applied voltage, as in Fig. XVI-6.

Determine the slope of the log plot whose reciprocal should be equal to 0.030, and the value of the half-wave potential of the cadmium ion in 0.2 N potassium chloride which should be about -0.60 volts vs. S.C.E.

CATHODIC REDUCTION OF BROMINE USING A ROTATING PLATINUM MICROELECTRODE[36]

Procedure. Prepare a supporting electrolyte that will be 0.05 N with respect to potassium bromide, and 1.0 N with respect to hydrochloric acid when the whole is diluted to 100 ml. volume. Add between 0.50 to 2.00 ml. of 0.001 N potassium bromate solution from a microburet. Dilute the entire solution to 100 ml.

Transfer the solution to a 125 ml. beaker and insert the beaker under the rotating platinum microelectrode assembly and the salt bridge providing contact with the external calomel reference electrode. Be sure that the microelectrode and the tip of the salt bridge are completely immersed in the solution. Turn on the motor and determine the current-voltage curve between +0.40 volts and -0.20 volts versus the S.C.E. Increase the potential of the microelectrode in steps of 0.01 to 0.02 volt. The bromine, liberated as a result of the reaction,

$$5\ Br^- + BrO_3^- + 6\ H^+ \rightarrow 3\ Br_2 + 3\ H_2O \quad (28)$$

is reduced to bromide ion at the electrode interface.

Repeat the experiment with a different volume of 0.001 N potassium bromate and determine whether the diffusion current is proportional to the concentration of bromine liberated. What regions of applied potential would be satisfactory for conducting an amperometric titration of arsenious oxide with potassium bromate?

POLAROGRAPHIC REDUCTION OF ORGANIC COMPOUNDS

Procedure. To a 100 ml. volumetric flask, add 25 ml. of a 0.10% aqueous solution of either methyl orange, orange II, or pontachrome blue black[37] R (plus 20 ml. acetone); 10 ml. of a 10% solution of sodium acetate, and 1 ml. of sulfuric acid diluted 1:9. Dilute the solution whose pH will be about 4.8 to the mark. Transfer 50 ml. of the solution to the electrolytic cell, remove the dissolved oxygen, and allow temperature equilibrium to be attained in a constant temperature bath.

After 15 minutes or longer, insert the electrolytic cell under the dropping mercury electrode assembly, being sure the capillary tip is completely immersed. Manually plot the current-voltage curve between 0.0 to -0.5 volt versus the S.C.E. in increments of 0.01 volt when the wave is developing, and every 0.05 volts preceding and succeeding the wave.

Repeat the above polarogram, after adding one additional milliliter of 1.9 sulfuric acid to the electrolytic cell, between 0.0 to -0.5 volts versus the S.C.E. To the remaining 50 ml. portion of the original solution, add 4 ml. of 1 N sodium hydroxide, remove the oxygen as before, and determine the polarogram between -0.1 to -0.6 volt vs. S.C.E.

Extrapolate the residual current curve and draw parallel to it a line through the diffusion current plateau. Draw a third line half-way between the two previous lines and parallel to them. The intersection of this line with the polarographic wave gives a rough value of the half-wave potential. Notice that the half-wave potential shifts to more negative values with increasing pH. Plot the three values of half-wave potentials thus obtained against the measured pH of the solution, and determine the slope of the resulting

36. Kolthoff, I. M. and Lingane, J. J., J. Phys. Chem., 45, 1085 (1941).

37. Color Index 202.

curve. Since the reduction involves two hydrogen ions and is reversible,

$$R - N = N - R + 2\,H^+ + 2\,e^- \rightarrow RNH - HNR \quad (29)$$

the half-wave potential of the system should be given by the following expression:

$$E = E^o + \frac{0.0591}{2} \log \frac{[R - N = N - R]}{[RNH - HNR]} + \frac{0.0591}{2} \log [H^+]^2 \quad (30)$$

$$E_{1/2} = E^o - 0.0591\ pH \quad (31)$$

THE POLAROGRAPHIC ANALYSIS OF COPPER-BASE ALLOYS[38]

Electrolysis at controlled cathode potential is used to remove the copper (and antimony, bismuth, etc.) prior to the determination of lead and tin in the residual solution in the presence of nickel and zinc. Iron is finally present in the ferrous state and does not interfere. Separate aliquot portions of the residual solution are used for lead in 1 N sodium hydroxide, and tin in a supporting electrolyte composed of 4 M ammonium chloride and 1 N hydrochloric acid.

Nickel and zinc are determined in a second sample after removal of copper, tin, and lead (and antimony, bismuth, etc.) by controlled cathode potential electrolysis. A supporting electrolyte composed of 0.2 M ammonium chloride and 1 M ammonium hydroxide is used. Small amounts of nickel may be determined accurately in the presence of large amounts of zinc.

In the supporting electrolyte chosen for tin, the stannic ion produces a double wave, corresponding to the stepwise reduction first to the stannous state and then to the metal. Either the first wave, the second wave alone, or the total double wave may be measured. The first wave and the total double wave involve corrections for the residual current, which must be determined separately because the first wave starts from zero applied potential; therefore the measurement of the second wave is recommended. The half-wave potential of lead in this supporting electrolyte is virtually coincident with that of the second state of the reduction of the chlorostannate ion, and hence the second wave includes a diffusion current due to lead for which a correction must be applied. As the amount of lead seldom exceeds the amount of tin, and usually is less, such a correction is not objectionable.

Procedure for Lead and Tin

Dissolve the sample of the alloy and electrolyze with controlled cathode potential as described under that topic to remove the copper. Transfer the residual solution to a 250 ml. volumetric flask, cool to room temperature, and dilute to the mark. The final solution will be about 0.4 N with respect to hydrochloric acid.

Lead. Transfer a 50 ml. aliquot to a 100 ml. volumetric flask, add 4.8 g., 0.12 mole, of sodi-

38. Lingane, J. J., Ind. Eng. Chem., Anal. Ed., 18, 429 (1946).

TABLE 1. PERTINENT HALF-WAVE POTENTIALS AND DIFFUSION CURRENT CONSTANTS

Temperature = 25° C. The half-wave potentials are referred to the saturated calomel electrode. The diffusion current constants correspond to the observed diffusion current in microamperes, when the concentration is 1 millimolar per liter, and when the value of $m^{2/3}t^{1/6}$ is 1 $mg^{2/3}sec^{-1/2}$. All solutions contained 0.005% gelatin.

Metal	Supporting Electrolyte		E 1/2 (volts)	I
Lead	1 M NaOH		-0.76	3.40
	4 M NH_4Cl + 1 M HCl		-0.52	3.52
Tin	4 M NH_4Cl + 1 M HCl	first	-0.25	2.84
		second	-0.52	3.49
		total		6.33
Nickel	0.2 M NH_4Cl + 1 M NH_4OH		-1.06	3.54
Zinc	0.2 M NH_4Cl + 1 M NH_4OH		-1.33	3.78

um hydroxide pellets, and 2.5 ml. of 0.2% gelatin solution, and dilute to the mark. Transfer a portion of the solution to the polarographic cell in a water thermostat at 25.0° ± 0.2° C., remove dissolved air with nitrogen or hydrogen, record the polarogram between -0.60 and -0.90 volt vs. S.C.E., and measure the diffusion current of the lead. Determine the m-value of the dropping electrode, measure the drop time at the potential at which the diffusion current was measured, and compute the concentration of lead from the relation, $C = i_d/3.40m^{2/3}t^{1/6}$.

Tin. Transfer another 50 ml. aliquot to a 100 ml. volumetric flask, add 21 g. of solid ammonium chloride, 6.6 ml. of 12 N hydrochloric acid, and 2.5 ml. of 0.2% gelatin solution, and dilute to about 90 ml. Shake until the ammonium chloride is dissolved, warm back to room temperature, and dilute to the mark. Transfer a portion of the solution to the polarographic cell in a water thermostat at 25.0° C., remove dissolved air with nitrogen or hydrogen, record the polarogram between -0.00 and -0.70 volt vs. S.C.E., and measure the diffusion current of the second wave. Apply the correction for lead, and compute the concentration of tin.

Notes: A large wave will be noticed in the lead analysis starting at zero applied potential due to the depolarization of the mercury cathode by the hydroxyl ions present. Neglect this wave, and use the diffusion current compensator to bring the galvanometer light back to zero at -0.60 volt vs. S.C.E.

The concentrations of the components in the supporting electrolytes are not critical, but should be within about 10% of the values specified.

To correct the diffusion current of the second or total tin wave for that of the lead wave, proceed as follows: From the data in Table 1 the diffusion current constant of lead in 4 M ammonium hydroxide - 1 M hydrochloric acid is seen to be larger than in 1 M sodium hydroxide, the ratio being 3.52/3.40 = 1.036. The contribution of lead to the second tin wave in the former medium was thus the diffusion current of lead in the sodium hydroxide medium, measured in microamperes, times 1.036 microamperes; and the diffusion current due to tin alone would be the total diffusion current measured in microamperes minus the above answer. The small difference in $m^{2/3}t^{1/6}$ values in the two media may be neglected.

Procedure for Nickel and Zinc. Dissolve a 0.5 g. sample, and prepare the solution for electrolysis, exactly as for the determination of lead and tin. Electrolyze first at a potential of -0.35 volt vs. S.C.E., and, after most of the copper is deposited, increase the potential to -0.70 volt to deposit tin and lead. Continue the electrolysis for about 10 minutes after the current decreases to a constant value. The current at -0.70 volt does not decrease to zero because hydrogen ion is reduced at this potential. Transfer the residual solution to a 250 ml. volumetric flask and dilute to the mark.

Since tin and lead are precipitated in the ammoniacal supporting electrolyte used for the determination of nickel and zinc, it is not essential that they be removed completely.

Transfer a 50 ml. aliquot to a 100 ml. volumetric flask, add 8 ml. of 15 M ammonia, 1 to 1.5 g. of pure anhydrous sodium sulfite to remove oxygen, and 2.5 ml. of 0.2% gelatin, and dilute to the mark. Place a portion of the solution in a polarographic cell in a water thermostat at 25.0° C., and record the polarogram between -0.80 and -1.60 volt vs. S.C.E. If the amount of nickel is much smaller than that of zinc, a second polarogram should be recorded at an increased sensitivity between -0.80 and -1.30 volt vs. S.C.E. to magnify the nickel wave to a value large enough for accurate measurement. Measure the two diffusion currents, the m-value of the capillary, and the drop times at the potentials at which the diffusion currents were measured. Compute the concentration of nickel from the diffusion current constant expression, and do the same for zinc.

A large diffusion wave will be noticed starting at zero applied potential as in the lead analysis. Use the diffusion current compensator to bring the galvanometer light back to zero at -0.80 volt.

Polarograms of some samples may show a final current increase at about -1.50 volts, which interferes with the full development of the diffusion current of the zinc. The interference can easily be eliminated by treating an aliquot of the electrolyzed solution with 5 ml. of concentrated nitric acid and evaporating to dryness to oxidize ferrous iron and hydroxylamine or hydrazine. The residue is taken up in an appropriate amount of dilute hydrochloric acid, and the solution is prepared for analysis as above.

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CHAPTER XVII

AMPEROMETRIC TITRATION METHODS

In addition to the two classical types of electrometric titrations already discussed - potentiometric and conductimetric - there may be added another, variously named amperometric, polarometric, or voltammetric titrations. The former name will be used henceforth to designate this class of titrations.

As has been shown in the previous chapter on Polarography, any substance able to depolarize a small indicator electrode will cause a definite limiting current to flow through the electrolytic solution. On a diffusion current plateau the limiting current is independent of the applied potential impressed upon the microelectrode because of the extreme state of concentration polarization existing at the surface of the microelectrode. The only factor affecting the limiting current, if the migration current is rendered negligible by adding sufficient inert electrolyte, is the rate of diffusion of electroactive material from the body of the solution to the electrode surface. Therefore, the diffusion current is proportional to the concentration of electroactive material in the solution. Now if a portion of the electroactive material should be removed through interaction with another reagent, the measured diffusion current will decrease. This is the basis for amperometric titrations; the observed diffusion current at a suitable applied voltage is measured as a function of the volume of titrating solution. The end point, as in conductimetry, is found as the point of intersection of two lines giving the change of current before and after the equivalence point.

If the current-voltage characteristics of the substance to be titrated and of the reagent are not known, it is always necessary first to determine the polarograms of both in the supporting electrolyte in which the titration is to be conducted. The applied voltage is then adjusted at the beginning of the titration to such a value that the total diffusion current of the substance to be titrated, or of the reagent, or of both, is obtained. This results in several types of titration curves as are illustrated in Figs. XVII-1b to XVII-4b. Above each titration graph, Figs. XVII-1a to XVII-4a, are shown the corresponding hypothetical current-voltage curves of each individual substance where X represents the polarogram of the solute to be titrated, and R is the polarogram of the titrating agent. For each amperometric titration the applied voltage was adjusted between the values A and B shown in Figs. XVII-1a to XVII-4a.

Thus Fig. XVII-2b might represent the titration of arsenite ions with standard bromate solution. The arsenite ions do not undergo an electrode reaction at any applied potential between A and B, whereas the diffusion current of the bromate ion (actually free bromine) is completely developed when the applied voltage is equal to A. Therefore, until the equivalence point is reached during the titration, only a small residual current will be flowing. But as soon as the first drop excess of bromate solution is added, the free bromine liberated by interaction with bromide present will undergo cathodic reduction at

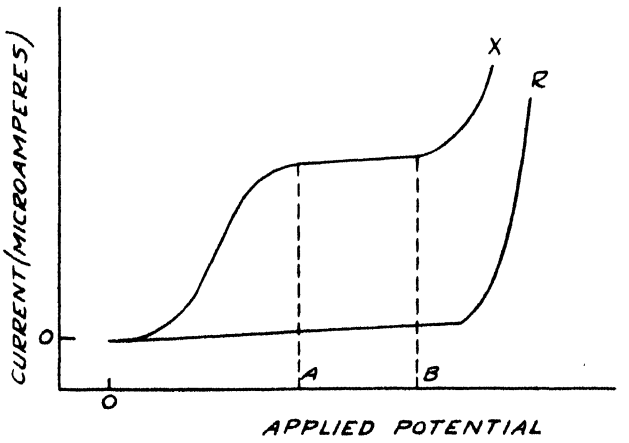

Fig. XVII-1a. Hypothetical current-voltage curves when only material being titrated (X) gives a diffusion current

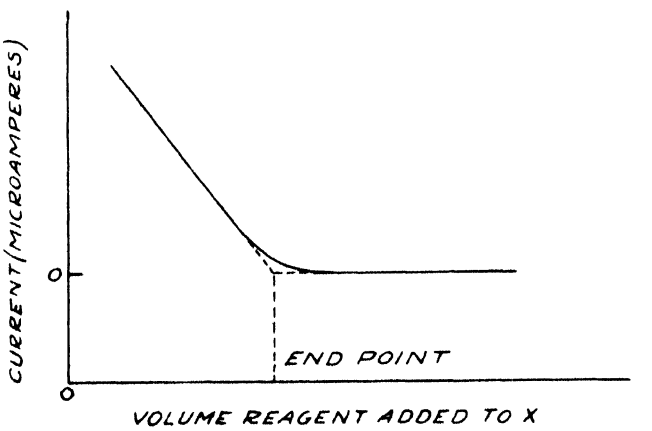

Fig. XVII-1b. Amperometric titration result for case 1a between applied voltages A to B

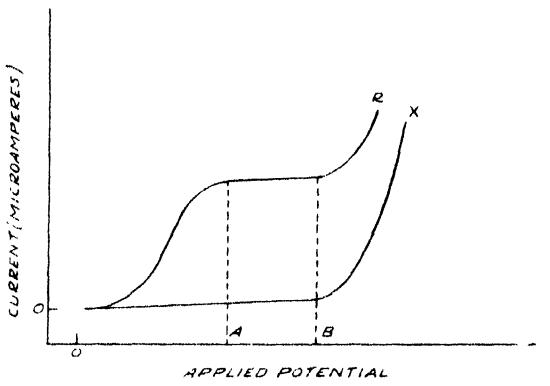

Fig. XVII-2a. Hypothetical current-voltage curves when only titrating agent (R) gives a diffusion current

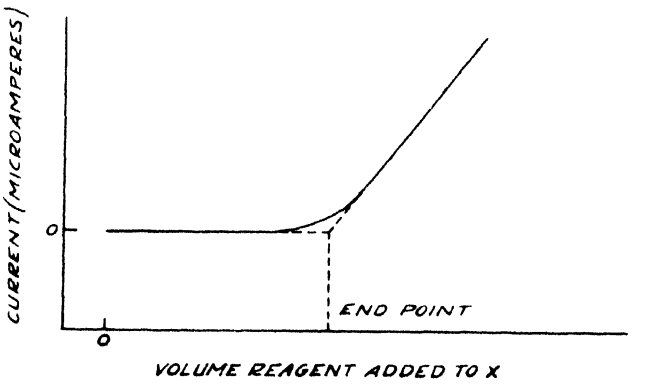

Fig. XVII-2b. Amperometric titration result for case 2a between applied potentials A to B

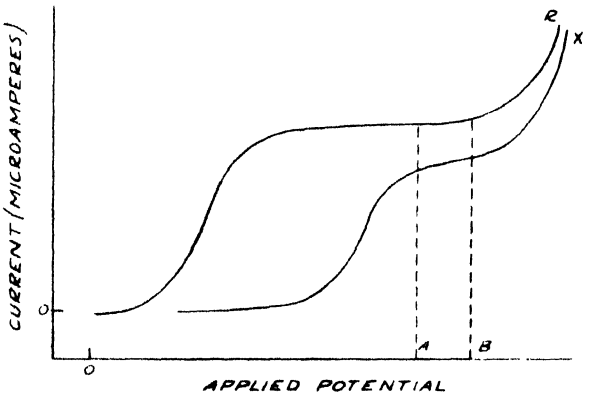

Fig. XVII-3a. Hypothetical current-voltage curves when both reactants gives diffusion currents

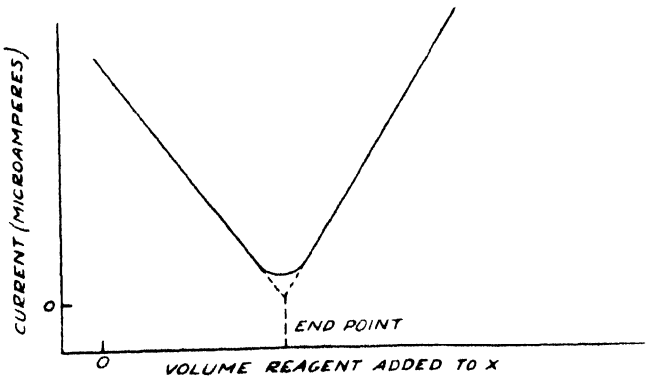

Fig. XVII-3b. Amperometric titration result for case 3a between applied potentials A to B

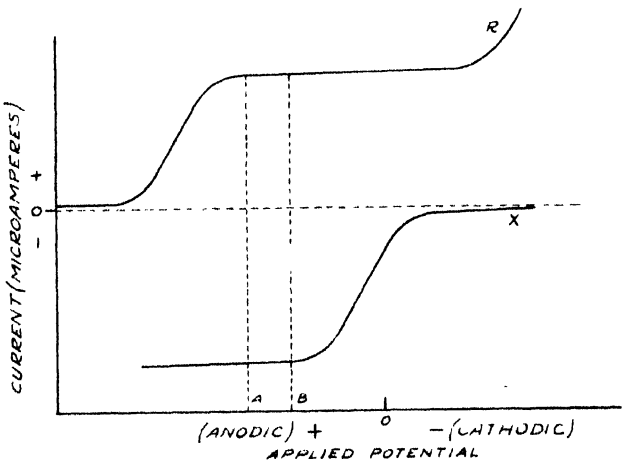

Fig. XVII-4a. Hypothetical current-voltage curves when one reactant gives an anodic diffusion current over similar applied potentials that the other reactant gives a cathodic diffusion current

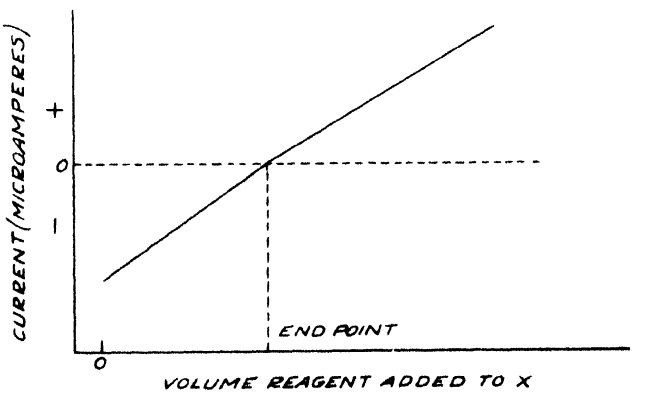

Fig. XVII-4b. Amperometric titration result for case 3b between applied potentials A to B

the electrode, and an increase in diffusion current will be noticed. Each additional drop thereafter of bromate solution will result in a corresponding increase in the observed diffusion current. A line drawn through about four points obtained after the equivalence point and intersecting with the initial residual current gives the volume of reagent used in the titration, from which value the amount of arsenite present in the sample can be calculated.

Similarly Fig. XVII-1b might represent the titration of lead ions which yield a diffusion current, with oxalate or sulfate ions which do not yield a diffusion current. The observed diffusion current will decrease steadily during the course of the titration until, at the equivalence point, and thereafter, only a small residual current will flow. If the reagent added during the titration also yields a diffusion current at the applied potential used, as might be the case when titrating lead with dichromate, the observed diffusion current will decrease until the equivalence point is reached, after which it will again rise due to the electrode reaction involving the excess dichromate ions. Fig. XVII-4b illustrates a titration curve which would be obtained when the substance being titrated gives an anodic diffusion current at the same applied potential as that at which the titrating agent gives a cathodic diffusion current. Examples include the titration of halide ions with mercuric ion and titration of titanous ions with ferric ions. Difficulty is experienced in determining the actual endpoint, which is at the point when the current is equal to the residual current.

To eliminate the necessity of correcting the observed diffusion currents for dilution, the reagent is added from a microburet in a concentration at least ten times that of the unknown. The migration current is eliminated by adding enough inert electrolyte; and, if necessary, a suitable maximum suppressor is also added.

Electrical Circuit. Any manually operated instrument available for determining the current-voltage curves could, obviously, be used in amperometric work. However, the applied potential need only be adjusted approximately in most instances, and therefore a battery and some kind of potential divider arrangement using a voltmeter will be an adequate source of potential. The remainder of the circuit consists of a current measuring device, either a microammeter or galvanometer and shunt, and the electrolytic cell. The manual circuit described in the laboratory section on Polarography is used in the authors' laboratory.

In some titrations the applied potential supplied by short-circuiting a standard reference cell will be sufficient to give the diffusion current of the electroactive ion, thus simplifying the experimental arrangement. Such an example is the titration of chloride or bromide ions with silver nitrate at zero applied potential,[1] when the cathode is short-circuited through a suitable current measuring device to a calomel reference electrode of relatively large area. Different potentials can be obtained by using different reference electrodes.

Types of Electrodes Used. Most of the work with amperometric titrations has been done using a dropping mercury indicator electrode. The titration cell must have provision for admission of the buret, dropping electrode, inert gas, and salt bridge. Nitrogen gas is passed through the solution for 15 minutes preceding the titration, and for a minute after the addition of each increment of reagent. In some instances it is simpler to remove any oxygen from the reagent and store it in the absence of air; even so the solution must be thoroughly stirred after each increment of reagent.

Because of the disadvantage of waiting after the addition of each increment of titrating agent until a steady state of diffusion current is obtained, it is more convenient to work with a rotating platinum microelectrode. Using the rotating platinum microelectrode the diffusion current is obtained instantly and has been found proportional to the concentration of electroactive substances in the reduction of iodine, bromine, chlorine, silver ion, and permanganate ion, and in the electro-oxidation of ferrous and ferrocyanide ions. In many instances, however, the greater current densities obtained with the rotating electrode do not permit the attainment of a complete concentration polarization, and, therefore, the currents observed will be disappointingly small. As a consequence optimum conditions must be determined for each particular ion before the rotating electrode may be applied, whereas usually any material which yields a polarogram can be titrated with suitable reagents if a dropping mercury electrode is used as the indicator electrode.

A typical microelectrode which has been frequently used consists of a platinum wire about 3 mm. long and 0.5 mm. in diameter, sealed into the side of a specially shaped bulb on the end of a piece of 8 mm. pyrex tubing. The tubing is mounted in the shaft of a motor or pulley which

1. Laitinen, H. A., Jennings, W. P., and T. D. Parks, Ind. Eng. Chem., Anal. Ed. 18, 355, 358 (1946).

is rotated at a speed of about 600 r.p.m. Electrical connection to the electrode is made by means of a piece of copper wire which dips into the column of mercury inside the tubing. If a motor chuck is used, a special flanged reservoir of mercury, into which the copper wire dips, serves as an external connection. The electrode must thoroughly stir the solution and rotate uniformly without creating turbulence along the electrode surface and thereby disturbing the diffusion layer.

A state of confusion exists in the literature concerning the effect of the rates of stirring of solutions on the rates of reactions at a solid-liquid interface. Very little work has been done on the subject; however, it seems that the diffusion current increases with approximately the 0.67th power of the rate of rotation of the microelectrode. This increased sensitivity is one major advantage of the rotating electrode. Recent results obtained in the authors' laboratory indicate that the diffusion current also is proportional to the area swept out by the electrode per second, as predicted by Fick's first law of diffusion.

In practically all the work an external reference electrode of large area, usually a saturated calomel, is used both for economy of mercury and convenience.

Reducible Gases. The current-voltage curves of oxygen reduction are of importance, since the limit of practical application is often determined by the efficiency with which the last traces of dissolved oxygen may be removed from the solution. The oxygen wave commences at about -0.4 volt vs. S.C.E. in an air-saturated solution. Oxygen removal by nitrogen requires at least 15 minutes, and the apparatus must be sealed from the air or a stream of carbon dioxide gas passed over the surface of the liquid. The removal of dissolved oxygen by reaction with sulfite is found to be efficient and rapid; 0.1 g. of sulfite per 100 ml. is sufficient.

Scope of the Method. Amperometric titrations are rapid and considerably more accurate than polarography. The method can be applied to a large variety of titrations involving neutralization, oxidation-reduction, and precipitation reactions. Even solutions as dilute as 0.0001 N can be titrated with fair precision. Neither titrant or material titrated need undergo a reversible electrode reaction as long as well-defined diffusion current is obtained. Even substances which themselves do not yield a diffusion current may be determined with a reagent, if the latter does give a diffusion current.

The results of the method are independent of the temperature, which must be maintained constant but at no definite value, of the capillary characteristics of dropping mercury electrodes, and of the concentration of any foreign material, as long as the half-wave potential of any foreign material does not interfere with that of the reagents. In a few instances, successive titrations of several constituents may be performed.

Particularly advantageous are the applications in precipitation reactions where good methods are lacking. Precipitations can be performed even when the solubility is relatively large, providing the solubility equilibrium is attained relatively quickly, since points of interest can be obtained considerably removed from the equivalence point where the solubility is repressed by the common-ion effect. Contrary to the conditions specified for conductometric titrations, foreign substances are actually beneficial.

In comparison to the potentiometric method, amperometric titrations are not as accurate, but considerably faster for more dilute solutions. Fair results are still obtained for concentrations of 0.0001 N, for which the potentiometric method is useless.

LABORATORY DIRECTIONS FOR AMPEROMETRIC TITRATION

Determination of Chromate. Chromate can be titrated with ferrous ion using the rotating platinum microelectrode as the anode, and measuring the anodic diffusion wave of the ferrous ion,[2] (Fig. XVIII-5). The method is accurate and can be used for concentrations as small as 0.0001 M

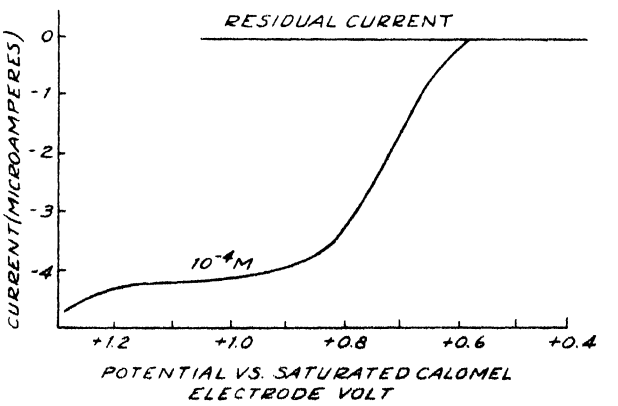

Fig. XVII-5. Current-voltage curves of ferrous ion in 0.1M H_3O^+ obtained with rotating platinum microelectrode

2. Kolthoff, I. M. and May, D. R., Ind. Eng. Chem., Anal. Ed., 18, 208 (1946).

chromate. The procedure can also be reversed to titrate ferrous iron with chromate.

Place the chromate sample of suitable size in a beaker, and place in position a rotating platinum electrode and salt bridge. A saturated calomel electrode is used as an external reference electrode. Add sufficient acid, either perchloric, hydrochloric, sulfuric, or nitric acid, to give a concentration of 0.1 M. Apply a 1 volt potential across the rotating anode and the external calomel electrode. Add a solution of ferrous ammonium sulfate, tenfold stronger than the chromate solution and 0.05 M in sulfuric acid, to the chromate sample from a microburette until a current is observed on the current measuring device. Rinse the sides of the beaker and record the diffusion current. Continue the addition of ferrous solution in increments of 0.05 ml., and measure the current after each addition until four or five readings have been taken. Plot the values and draw a line connecting the points obtained after the equivalence point until it intersects the residual current line. Read the volume of titrant used and calculate the concentration of chromate present in the sample.

Determination of Arsenious Oxide with Bromate.[3] The unknown arsenite solution is placed in a beaker of suitable size. Sufficient hydrochloric acid and potassium bromide are added to make the solution 1 N with respect to the acid and 0.05 N in bromide. A rotating platinum microelectrode is used as an indicator electrode and a saturated calomel electrode, as a reference electrode, an e.m.f. of 0.2 to 0.3 volt being applied across the platinum anode and saturated calomel electrode. The current remains practically equal to zero in the presence of an excess of arsenious oxide and increases with an excess of bromate, the current being proportional to the bromate (actually free bromine) concentration. The bromate is added to the arsenite solution from a microburette. When a deflection of the galvanometer is noticed, the buret is closed, and the readings of the buret and current are recorded. Small increments of bromate are then added and the current recorded after each addition.

Solutions 0.001 N in arsenic can be titrated with an accuracy of 0.1%. Even solutions 0.0001 N can be titrated with an accuracy and precision of 0.3%

Determination of Lead with Dichromate.[4] In this titration both the lead and chromate ions yield a diffusion current at an applied cathodic potential of -1.0 volt vs. S.C.E. Only a dropping mercury electrode will yield satisfactory diffusion currents.

Transfer 50 ml. of 0.01 M lead nitrate and 10 ml. of 0.1 N potassium nitrate to a closed electrolytic cell. Remove the dissolved oxygen by bubbling nitrogen through the solution for 15 minutes. Insert the dropping mercury assembly and salt bridge. Set the applied potential at -1.0 volt vs. S.C.E., and begin the flow of mercury from the capillary. Slowly add 0.05 M potassium dichromate from a microburet. After each addition, pass nitrogen through the solution for 1 minute to remove oxygen and to mix the solutions, then measure the current. Repeat this procedure until four or five points have been obtained before and after the equivalence point. An initial current of perhaps 100 microamperes will decrease during the course of the titration to a small value at the equivalence point, and then rise again beyond the equivalence point. Draw lines through the two series of points until they intersect giving the volume of 0.05 M potassium dichromate used to reach the equivalence point.

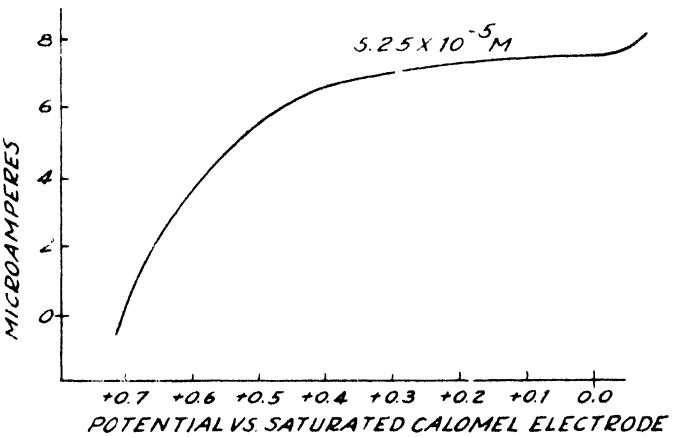

Fig. XVII-6. Current-voltage curve of Bromine in 1N HCl and 0.05 M K Br obtained with rotating platinum microelectrode

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3. Laitinen, H. A. and Kolthoff, I. M., J. Phys. Chem., 45, 1090 (1941).

4. Kolthoff, I. M. and Pan, Y. D., J. Am. Chem. Soc., 61, 3402 (1939).

APPENDIX

TABLE I. OXIDATION-REDUCTION POTENTIALS

(The numerical values are from "Oxidation Potentials," by W. M. Latimer, copyright 1938 by Prentice-Hall, New York, and reproduced here with permission.)

Couple	E^o
$Li = Li^+ + e$	-3.02
$K = K^+ + e$	-2.92
$Ba = Ba^{++} + 2e$	-2.90
$Sr = Sr^{++} + 2e$	-2.89
$Ca = Ca^{++} + 2e$	-2.87
$Na = Na^+ + e$	-2.71
$La = La^{+++} + 3e$	-2.37
$Mg = Mg^{++} + 2e$	-2.34
$Ti = Ti^{++} + 2e$	-1.75
$Be = Be^{++} + 2e$	-1.70
$Al = Al^{+++} + 3e$	-1.67
$Mn = Mn^{++} + 2e$	-1.05
$Zn = Zn^{++} + 2e$	-0.762
$H_2O + H_3PO_2 = H_3PO_3 + 2H^+ + 2e$	-0.59
$H_2C_2O_4\ (aq) = 2CO_2(g) + 2H^+ + 2e$	-0.49
$Fe = Fe^{++} + 2e$	-0.44
$H_2 = 2H^+(10^{-7}\ M) + 2e$	-0.414
$Cr^{++} = Cr^{+++} + e$	-0.41
$Cd = Cd^{++} + 2e$	-0.40
$Co = Co^{++} + 2e$	-0.277
$Ni = Ni^{++} + 2e$	-0.250
$2H_2O + HS_2O_4^- = 2H_2SO_4 + H^+ + 2e$	-0.23
$I^- + Ag = AgI + e$	-0.151
$Sn = Sn^{++} + 2e$	-0.136
$Pb = Pb^{++} + 2e$	-0.126
$2NH_3OH^+ = N_2O + H_2O + 6H^+ + 4e$	-0.05
$4I^- + Hg = HgI_4^{--} + 2e$	-0.04
$H_2 = 2H^+ + 2e$	0.000
$Br^- + Ag = AgBr + e$	0.073
$Co(NH_3)_6^{++} = Co(NH_3)_6^{+++} + e$	0.10
$H_2S = S + 2H^+ + 2e$	0.14
$Sn^{++} = Sn^{+4} + 2e$	0.15
$Cu^+ = Cu^{++} + e$	0.167
$2S_2O_3^{--} = S_4O_6^{--} + 2e$	0.17
$2Cl^- + Cu = CuCl_2^- + e$	0.19
$H_2O + H_2SO_3 = SO_4^{--} + 4H^+ + 2e$	0.20
$Sb + H_2O = SbO^+ + 2H^+ + 3e$	0.212
$Cl^- + Ag = AgCl + e$	0.2222
$2Cl^- + 2Hg = Hg_2Cl_2 + 2e$	0.2676
$H_2O + Bi = BiO^+ + 2H^+ + 3e$	0.32
$Cu = Cu^{++} + 2e$	0.345
$Fe(CN)_6^{-4} = Fe(CN)_6^{---} + e$	0.36
$2NH_3(aq) + Ag = Ag(NH_3)_2^+ + e$	0.37
$2I^- = I_2 + 2e$	0.5345

Couple	E^o
$2H_2O + HAsO_2 = H_3AsO_3 + 2H^+ + 2e$	0.559
$CuCl = Cu^{++} + Cl^- + e$	0.566
$SO_4^{--} + 2Hg = Hg_2SO_4 + 2e$	0.6151
$H_2O_2 = O_2 + 2H^+ + 2e$	0.68
$Fe^{++} = Fe^{+++} + e$	0.771
$2Hg = Hg_2^{++} + 2e$	0.7986
$Ag = Ag^+ + e$	0.7995
$2H_2O = O_2 + 4H^+(10^{-7}\ M) + 4e$	0.815
$Hg = Hg^{++} + 2e$	0.854
$HNO_2 + H_2O = NO_3^- + 3H^+ + 2e$	0.94
$2H_2O + NO = NO_3^- + 4H^+ + 3e$	0.96
$3H_2O + VO^{++} = V(OH)_4^+ + 2H^+ + e$	1.000
$3H_2O + I^- = IO_3^- + 6H^+ + 6e$	1.085
$2Br^- = Br_2(aq) + 2e$	1.087
$Pt = Pt^{++} + 2e$	ca 1.2
$2H_2O = O_2 + 4H^+ + 4e$	1.229
$Cl^- = 1/2Cl_2 + e$	1.[illegible]8
$7H_2O + 2Cr^{+++} = Cr_2O_7^{--} + 14H^+ + 6e$	1.36
$3H_2O + Br^- = BrO_3^- + 6H^+ + 6e$	1.44
$4H_2O + Mn^{++} = MnO_4^- + 8H^+ + 5e$	1.52
$Ce^{+3} = Ce^{+4} + e$	1.61

TABLE II. DEFINITION AND RELATION OF IMPORTANT RADIANT ENERGY UNITS

Wavelength, λ	
Ångström, Å or .U.	= 1/6438.4696 of the wavelength of the Cd red line.
	= meters x 10^{-10} = 10^{-8} cm.
Millimicron, mμ	= 10^{-7} cm. = 10 Å.
Micron, μ	= 10^{-3} mm. = 10,000 Å.
	= 1000 mμ
X.U.	= 10^{-11} cm. = 10^{-3} Å.
Wave number, ν' or $\bar{\nu}$	
Waves per centimeter	= $cm^{-1} = \frac{1}{\lambda}$
	= $\frac{10^{-7}}{m\mu}$
Frequency, ν	
Vibrations per second	= $\frac{c}{\lambda} = \frac{3 \times 10^{-10}}{\lambda}$
Fresnel, f	= $10^{-12}\ \nu$
	= $0.03\ \nu'$
	= $\frac{3 \times 10^{-5}}{m\mu} = \frac{3 \times 10^6}{Å}$

'ABLE III. RELATION OF COLOR, WAVELENGTH, FREQUENCY, AND WAVE NUMBER

λ Wavelength ($m\mu$)	Color	ν Frequency (fresnel)	ν' Wave number (cm^{-1})
28,000		10.7	357
	Near Infrared (Analytical range)		
1,000		300	10,000
750		400	13,340
	Red		
620		484	16,140
	Orange		
600		500	16,670
	Yellow		
580		517	17,240
	Green		
500		600	20,000
	Blue		
440		682	22,750
	Violet		
400		750	25,000
	Near Ultraviolet (Analytical range)		
230		1305	43,500
	Far Ultraviolet		

TABLE IV. DISSOCIATION CONSTANTS OF SOME ACIDS AND BASES

Acids	K_a	pK_a
Acetic Acid	1.75×10^{-5}	4.76
Boric Acid	6.6×10^{-10}	9.18
Boric Acid with Glycerine	3×10^{-7}	6.52
Carbonic Acid, First Step	3.0×10^{-7}	6.52
Second Step	4×10^{-11}	10.4
Citric Acid, First Step	8.2×10^{-4}	3.09
Second Step	1.8×10^{-5}	4.75
Third Step	3.9×10^{-7}	6.41
Oxalic Acid, First Step	3.8×10^{-2}	1.42
Second Step	6.1×10^{-5}	4.21
Nitrous Acid	4×10^{-4}	3.4
Phenol	1.3×10^{-10}	9.89
Phosphoric Acid, First Step	1.1×10^{-2}	1.96
Second Step	7.5×10^{-8}	7.13
Third Step	5×10^{-13}	12.3
Phthalic Acid, First Step	1.26×10^{-3}	2.90
Second Step	3.9×10^{-6}	5.41
Sulfanilic Acid	6.3×10^{-4}	3.2
Hydrogen Sulfide, First Step	5.7×10^{-8}	7.24
Second Step	1.2×10^{-15}	14.9

Bases	K_b	pK_b
Ammonium Hydroxide	1.75×10^{-5}	4.76
Aniline	3.5×10^{-10}	9.46
Ethylamine	5.6×10^{-4}	3.25
Ethanolamine	ca. 10^{-3}	3.0
Hydrazine	3×10^{-6}	5.5
Hydroxylammonium Hydroxide	6.6×10^{-9}	8.18

TABLE V. HALF-WAVE POTENTIALS*

(Values listed are in volts vs. the saturated calomel electrode at 25°C. 0.01% gelatin present in all cases)

Supporting Electrolyte	Cu	Bi	Sb	Sn II	Sn IV	Pb	Ni	Cd	Cr III	Cr VI	Zn
0.1 N KCl	+0.04	Ins.[d]	Ins.[d]	Ins.[d]	Ins.[d]	-0.04	-1.1	-0.60	-0.88 -1.53	-1.0 -1.5 -1.7	-1.00
0.1 N HCl	+0.04 -0.22	-0.09	-0.15	-0.47	-0.47	-0.43		-0.64			a
1 N H_2SO_4	0.0	-0.04	-0.46	-0.46	Ins.[d]	Ins.[d]		-0.59			a
1 N HNO_3	-0.01	-0.01	-0.30	-0.44	Ins.[d]	-0.40		-0.59			a
1 N NaOH	-0.42	Ins.[d]	-1.26	-0.73[c]	N.R.[b]	-0.76		Ins.[d]	-0.85		-1.50
Acidic Tartrate	-0.09	-0.29	-0.8	-0.20[c]	N.R.[b]	-0.48		-0.64		-1.02	-1.23
1 N NH_4Cl + 1 N NH_4OH	-0.24 -0.50	Ins.[d]	Ins.[d]	Ins.[d]	Ins.[d]	Ins.[d]	-1.09	-0.81	-0.35 -1.7		-1.36
4 N NH_4Cl + 1 N HCl				-0.52	-0.25	-0.52					

a. Wave masked by final current increase.
b. Not reduced at the dropping electrode.
c. Anodic wave.
d. Ins. stands for "insoluble."

*Taken from J. J. Lingane, Ind. Eng. Chem., Anal. Ed., 15, 584 (1943).

TABLE VI. DIFFUSION CURRENT CONSTANTS*

(Values listed are $i_d/(Cm^{2/3}t^{1/6})$ at 25.0°C. In all cases 0.01% gelatin was present as maximum suppressor. Values in parentheses are uncertain because of poorly defined diffusion currents)

Supporting Electrolyte	Cu	Bi	Sb	Sn II	Sn IV	Pb	Ni	Cd	Zn
0.1 N KCl	3.23					3.80		3.51	3.42
1 N HCl	3.39	5.23	5.54	4.07	(4.8)	3.86		3.58	
1 N H_2SO_4	(2.12)	4.31	4.94	3.54				(2.6)	
1 N HNO_3	3.25	4.64	5.10	4.02		3.67		3.06	
1 N NaOH	2.91		4.54	3.45		3.85			3.14
Acidic Tartrate	2.37	3.12	(3.4)	2.41		2.37		2.34	
1 N NH_4Cl + 1 N NH_4OH	3.75						3.56	3.68	3.82
4 N NH_4Cl + 1 N HCl				3.49	2.84	3.52			

*Taken from J. J. Lingane, Ind. Eng. Chem., Anal. Ed., 15, 589 (1943).

TABLE VII. SCALE READINGS ON ZEISS IMMERSION REFRACTOMETER AT 20°C. CORRESPONDING TO EACH PER CENT. BY WEIGHT OF ETHYL AND METHYL ALCOHOL*

% Alcohol by Weight	Scale readings		% Alcohol by Weight	Scale readings		% Alcohol by Weight	Scale readings	
	Methyl Alcohol	Ethyl Alcohol		Methyl Alcohol	Ethyl Alcohol		Methyl Alcohol	Ethyl Alcoho
0 . . .	14.5	14.5	34 . . .	35.2	74.4	68 . . .	34.0	99.4
1 . . .	14.8	16.0	35 . . .	35.8	75.8	69 . . .	33.5	99.
2 . . .	15.4	17.6	36 . . .	36.3	76.9			
3 . . .	16.0	19.1	37 . . .	36.8	78.0	70 . . .	33.0	100.
4 . . .	16.6	20.7	38 . . .	37.3	79.1	71 . . .	32.3	100.
5 . . .	17.2	22.3	39 . . .	37.7	80.2	72 . . .	31.7	100.
6 . . .	17.8	24.1				73 . . .	31.1	100.
7 . . .	18.4	25.9	40 . . .	38.1	81.3	74 . . .	30.4	100.
8 . . .	19.0	27.8	41 . . .	38.4	82.3	75 . . .	29.7	101.
9 . . .	19.6	29.6	42 . . .	38.8	83.3	76 . . .	29.0	101.
			43 . . .	39.2	84.2	77 . . .	28.3	100.
10 . . .	20.2	31.4	44 . . .	39.3	85.2	78 . . .	27.6	100.
11 . . .	20.8	33.2	45 . . .	39.4	86.2	79 . . .	26.8	100.8
12 . . .	21.4	35.0	46 . . .	39.5	87.0			
13 . . .	22.0	36.9	47 . . .	39.6	87.8	80 . . .	26.0	100.7
14 . . .	22.6	38.7	48 . . .	39.7	88.7	81 . . .	25.1	100.6
15 . . .	23.2	40.5	49 . . .	39.8	89.5	82 . . .	24.3	100.5
16 . . .	23.9	42.5				83 . . .	23.6	100.4
17 . . .	24.5	44.5	50 . . .	39.8	90.3	84 . . .	22.8	100.
18 . . .	25.2	46.5	51 . . .	39.7	91.1	85 . . .	21.8	100.
19 . . .	25.8	48.5	52 . . .	39.6	91.8	86 . . .	20.8	99.
			53 . . .	39.6	92.4	87 . . .	19.7	99.
20 . . .	26.5	50.5	54 . . .	39.5	93.0	88 . . .	18.6	99.
21 . . .	27.1	52.4	55 . . .	39.4	93.6	89 . . .	17.3	98.9
22 . . .	27.8	54.3	56 . . .	39.2	94.1			
23 . . .	28.4	56.3	57 . . .	39.0	94.7	90 . . .	16.1	98.6
24 . . .	29.1	58.2	58 . . .	38.6	95.2	91 . . .	14.9	98.3
25 . . .	29.7	60.1	59 . . .	38.3	95.7	92 . . .	13.7	97.8
26 . . .	30.3	61.9				93 . . .	12.4	97.2
27 . . .	30.9	63.7	60 . . .	37.9	96.2	94 . . .	11.0	96.5
28 . . .	31.6	65.5	61 . . .	37.5	96.7	95 . . .	9.6	95.7
29 . . .	32.2	67.2	62 . . .	37.0	97.1	96 . . .	8.2	94.9
			63 . . .	36.5	97.5	97 . . .	6.7	94.0
30 . . .	32.8	69.0	64 . . .	36.0	98.0	98 . . .	5.1	93.0
31 . . .	33.5	70.4	65 . . .	35.5	98.3	99 . . .	3.5	92.0
32 . . .	34.1	71.7	66 . . .	35.0	98.7			
33 . . .	34.7	73.1	67 . . .	34.5	99.1	100 . . .	2.0	91.0

*Taken from Leach and Lythgoe, J. Am. Chem. Soc., 27, 964 (1905).

TABLE VIII. COMMON LOGARITHMS OF NUMBERS

(To four decimal places)

Natural numbers	0	1	2	3	4	5	6	7	8	9	Proportional Parts 1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0204	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1793	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4592	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4880	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5052	5066	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	5	8	9	10	12
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6242	6253	6263	6274	6284	6294	6304	6214	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6285	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	8
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

TABLE VIII (Cont.)

Natural numbers	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7597	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	5	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	5	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	5	5	6	7
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	5	5	6	7
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8359	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9145	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9279	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9335	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9745	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

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- B -